Foreword

This collection of problems and solutions is intended to aid students taking our course in Solid State Physics. Exercises are an integral part of a course and the reader is urged to attempt most of them. The problems are selected from areas usually covered in a first course and are of a type most often assigned for class work and given on examinations. No arrangement in order of complexity has been attempted and for some problems only answers are given.

Luleå, Sweden
January 1995 Sune Marklund

The layout and chapters division have been changed. Some problems have also been added or changed and some solutions are elucidated.

Luleå, Sweden
February 1996 Niklas Lehto

Chapters containing some problems on superconductivity, on optical and dielectric properties, and on magnetic properties have been added.

Luleå, Sweden
February 1997 Niklas Lehto

A section on X–ray diffraction has been added. The section is based on 'Elementary Solid State Physics' by M. Ali Omar. Addison Wesley. The intention is to supplement Kittel (ed. 7) chapter 2.

Luleå, Sweden
February 2000 Hans Weber

Three laboratory excersises have been added.

Luleå, Sweden
February 2001 Hans Weber

Minor corrections.

Luleå, Sweden
February 2003 Hans Weber

Contents

Foreword **i**

A X-ray diffraction **1**
1 Scattering from an atom . . . 1
2 Scattering from an crystal . . . 5
3 The reciprocal lattice and X–ray diffraction . . . 8
4 The diffraction condition and Bragg's law . . . 13

B Problems in Solid State Physics **17**
1 Crystal Structures . . . 17
2 The Reciprocal Lattice . . . 19
3 Diffraction in Crystals . . . 20
4 Crystal Binding . . . 22
5 Lattice Vibrations . . . 23
6 The Free Electron Model . . . 25
7 Band Theory . . . 27
8 Semiconductors . . . 29
9 Superconductivity . . . 31
10 Optical and Dielectric Properties . . . 32
11 Magnetic Properties . . . 33

C Solutions, Hints or Answers **35**
1 Crystal Structures . . . 35
2 The Reciprocal Lattice . . . 36
3 Diffraction in Crystals . . . 40
4 Crystal Binding . . . 43
5 Lattice Vibrations . . . 46
6 The Free Electron Model . . . 51
7 Band Theory . . . 54
8 Semiconductors . . . 56
9 Superconductivity . . . 59
10 Optical and Dielectric Properties . . . 60
11 Magnetic Properties . . . 61

D Lab: X – Ray Crystallography **65**
1 Purpose . . . 65
2 Literature . . . 65

3 X–ray diffraction, some general principles . . . 65
3.1 Bragg law . . . 65
3.2 Miller indices . . . 67
3.3 Spacing between planes of the same Miller indices. . . . 68
4 Diffraction conditions . . . 69
4.1 Reciprocal lattice . . . 69
4.2 The structure factor of some cubic lattices . . . 70
5 Equipment and safety . . . 71
5.1 X–ray equipment and safety . . . 71
5.2 The Geiger–Müller counter . . . 73
6 Calculations and lab work . . . 74
7 Crystal structure . . . 75
8 Credits . . . 77

E Lab: Electrons in periodic potentials, Band structure of crystals 79
1 Purpose . . . 79
2 Literature . . . 79
3 Background . . . 79
4 Electron in a periodic potential . . . 81
5 Preparing for Work . . . 84
6 Work . . . 85
7 Appendix: Time independent perturbation calculation . . . 88
8 Credits . . . 89

F Lab: Magnetism 91
1 Purpose . . . 91
2 Literature . . . 91
3 Magnetic properties . . . 91
4 Diamagnetism . . . 92
5 Paramagnetism . . . 92
6 Gouy's method . . . 93
7 Doing the experiment . . . 95

A

X-ray diffraction

The text in this chapter is based on 'Elementary Solid State Physics' by M. Ali Omar. The book is no longer available.

1 Scattering from an atom

The diffraction process can be divided naturally into two stages: (1) scattering by individual atoms, and (2) mutual interference between the scattered rays. Since the two stages are distinct from each other, we shall treat them independently, for convenience.

Why does an atom scatter the x–ray beam? Well, any atom is surrounded by electrons which undergo acceleration under the action of the electric field associated with the beam. Since an accelerated charge emits radiation (a fact well known from electromagnetism), so do the atomic electrons. In effect the electrons absorb energy from the beam, and scatter it in all directions. But the electrons form a charge cloud surrounding the atom, so when we are considering scattering from the atom as a whole, we must take into account the phase differences between the rays scattered from the different regions of the charge cloud. We do this as follows: Consider a single electron, as shown in Fig A.1a. A plane–wave field given by

$$u = Ae^{i(\mathbf{k_0}\cdot\mathbf{r}-\omega t)}$$

is incident on the electron, where A is the amplitude, $\mathbf{k_0}$ the wave vector ($k_0 = 2\pi/\lambda$), and ω the angular frequency. The scattered field is an outgoing spherical wave represented by

$$u' = f_e \frac{A}{D} e^{i(kD-\omega t)} \tag{A.1}$$

where f_e is the *scattering length* of the electron, and D is the radial distance from the electron to the point at which the field is evaluated. The quantity k is the wave number of the scattered wave, and has the same magnitude as k_0. Note the the amplitude of the scattered wave decreases with distance as $1/D$, a property shared by all spherical waves.

Suppose now that the incident wave acts on two electrons, as in Fig A.1b. In this case, both electrons emit spherical waves, and the scattered field observed at a distant point is the sum of the two partial fields, where their phase difference has to be taken into account. Thus we have

$$u' = f_e \frac{A}{D}\left[e^{ikD} + e^{ikD+\delta}\right] \tag{A.2}$$

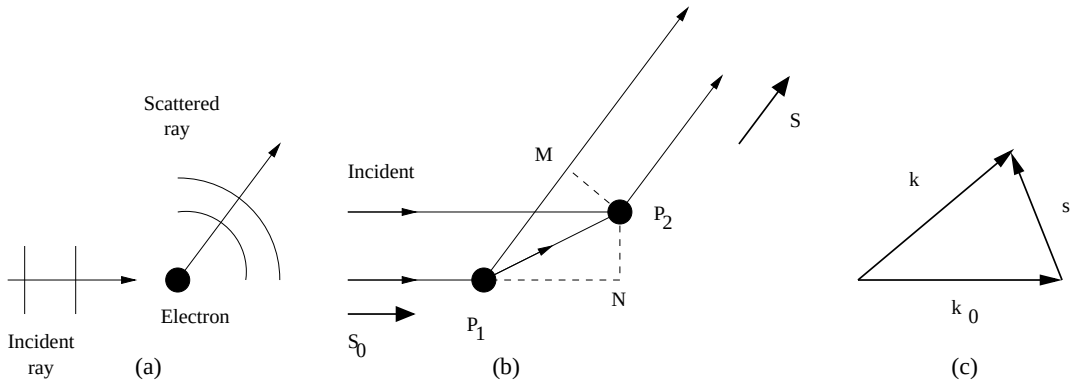

Figure A.1: Scattering from (a) a single electron, (b) two electrons. (c) The scattering vector **s**. Note that the vectors $\mathbf{k_0}, \mathbf{k}$, and **s** form an isosceles triangle.

where δ is the phase lag of the wave from electron 1 behind that of electron 2 [1]. (The time factor has been omitted for the sake of brevity, but its presence is implied.) Referring to the figure, we may write

$$\delta = (P_1M - P_1N)\, 2\pi/\lambda = (\mathbf{r}\cdot\mathbf{S} - \mathbf{r}\cdot\mathbf{S_0})\, k$$

where **r** is the vector radius of electron 2 relative to electron 1, and $\mathbf{S_0}$ and **S** are the unit vectors in the incident and scattered directions, respectively. The expression for δ can be set forth in the form

$$\delta = \mathbf{s}\cdot\mathbf{r}, \tag{A.3}$$

where the scattering vector **s** is defined as

$$\mathbf{s} = k\,(\mathbf{S} - \mathbf{S_0}) = \mathbf{k} - \mathbf{k_0}. \tag{A.4}$$

As seen from Fig A.1c, the magnitude of the scattering vector is given by

$$s = 2k\sin(\theta) \tag{A.5}$$

where θ is half of the scattering angle. Substituting the expression Eq (A.3) for δ into Eq. (A.2), one finds

$$u' = f_e\frac{A}{D}e^{ikD}\left[1 + e^{i\mathbf{s}\cdot\mathbf{r}}\right] \tag{A.6}$$

In deriving this we have chosen the origin of our coordinates at electron 1. But it is now more convenient to choose the origin at an arbitrary point, and in this manner treat the two electrons on equal footing. The ensuing expression for the scattered field is then

$$u' = f_e\frac{A}{D}e^{ikD}\left[e^{i\mathbf{s}\cdot\mathbf{r_1}} + e^{i\mathbf{s}\cdot\mathbf{r_2}}\right] \tag{A.7}$$

where $\mathbf{r_1}$ and $\mathbf{r_2}$ are the position vectors of the two electrons relative to a new origin. Equation (A.6) is a special case of (A.7), where $\mathbf{r_1} = 0$, that is, where the origin is chosen

[1] The distance D to the field point is assumed to be large, otherwise the denominator D in Eq. (A.2) would not be the same for the two electrons. This conditions simplifies the calculations, and is the reason why the detector is usually placed far from the crystal

at electron 1, as pointed out above. The generalisation of (A.7) to an arbitrary number of scatterers is now immediate, and the result is

$$u' = f_e \frac{A}{D} e^{ikD} \sum_l e^{i\mathbf{s}\cdot\mathbf{r}_l}$$

where $\mathbf{r}_l$ is the position of the lth electron, and the sum is carried out over all the electrons. By analogy with the case of the single electron, equation (A.1), the scattering length for the system as a whole is now given by the sum

$$f = f_e \sum_l e^{i\mathbf{s}\cdot\mathbf{r}_l}. \tag{A.8}$$

That is, the total scattering length is the sum of individual lengths with the phases taken properly into account. The intensity I of the scattered beam is proportional to the square of the magnitude of the field, and therefore

$$I \sim \mid f \mid^2 = f_e^2 \mid \sum_l e^{i\mathbf{s}\cdot\mathbf{r}_l} \mid^2 . \tag{A.9}$$

Results (A.8) and (A.9) are the basic equations in the treatment of scattering and diffraction processes, and we shall use them time and again in the following pages.

We may digress briefly to point out an important aspect of the scattering process: the *coherence* property involved in the scattering. This property means that the scatterers maintain definite phase relationships with each other. Consequently we can speak of interference between the partial rays. By contrast, if the scatterers were to oscillate randomly, or incoherently, the partial rays would not interfere, and the intensity at the detector would simply be the sum of the partial intensities, that is,

$$I \sim N f_e^2,$$

where N is the number of scatterers. Note the marked difference between this result and that of coherent scattering in eq. (A.9).

The scattering length of the electron is well known , and can be found in books on electromagnetism. Its value is

$$f_e = \left[\left(1 + \cos^2(2\theta)\right)/2\right]^{1/2} r_e,$$

where r_e, the so–called classical radius of the electron, has a value of about 10^{-15}m. [2]

We can now apply these results to the case of a single free atom. In attempting to apply eq. (A.8), where the sum over the electrons appears, we note that the electrons do not have discrete positions, but are spread as a continuous charge cloud over the volume of the atom. It is therefore necessary to convert the discrete sum to the corresponding integral. This readily leads to

$$f = f_e \sum_l e^{i\mathbf{s}\cdot\mathbf{r}_\mathbf{l}} \rightarrow f_e \int \rho(\mathbf{r}) e^{i\mathbf{s}\cdot\mathbf{r}} d^3r,$$

[2]For the sake of visual thinking, consider the electron to be in the form of a sphere whose radius is roughly equal to the scattering length f_e. Thus the electron "appears" to the radius as a circular obstacle of cross section πf_e^2.

where $\rho(\mathbf{r})$ is the density of the cloud (in electrons per unit volume), and the integral is over the atomic volume. The *atomic scattering factor* f_a is defined as the integral appearing in the above expression, i.e,

$$f_a = \int \rho(\mathbf{r}) e^{i\mathbf{s}\cdot\mathbf{r}} d^3r,$$

(Note that f_a is a dimensionless quantity.) The integral can be simplified when the density $\rho(\mathbf{r})$ is spherically symmetric about the nucleus, because then the integration over the angular part of the element of volume can be readily performed. The resulting expression is

$$f_a = \int_0^R 4\pi r^2 \rho(r) \frac{\sin sr}{sr} dr, \tag{A.10}$$

where R is the radius of the atom (the nucleus being located at the origin). As seen from eq. (A.10), the scattering factor f_a depends on the scattering angle (recall that $s = 2k\sin\theta$), and this comes about from the presence of the oscillating factor $(\sin sr)/sr$ in the integrand. The wavelength of oscillation is inversely proportional to s in Fig A.2a, and the faster the oscillation – i.e., the shorter the wavelength – the smaller is f_a, due to the interference between the partial beams scattered by different regions of the charge cloud. Recalling that $s = 2k\sin\theta$, Eq (A.5), we see that as the scattering angle 2θ increases, so also does s, and this results in a decreasing scattering factor f_a.

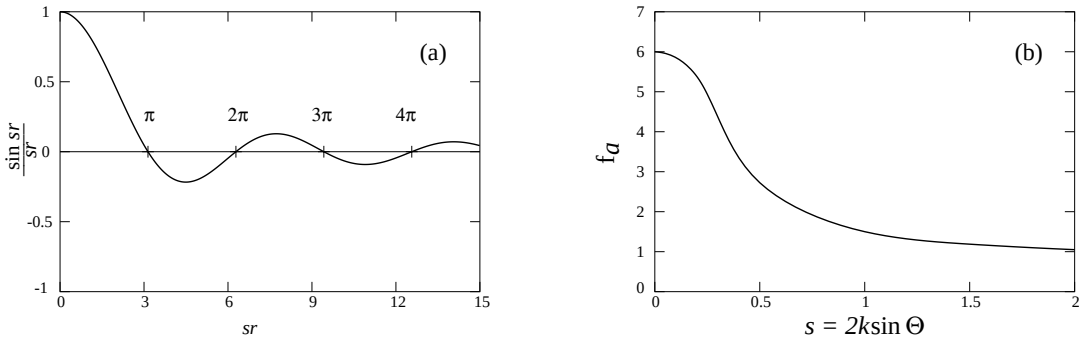

Figure A.2: (a) Oscillating factor $(\sin sr)/sr$. (b) Atomic scattering factor for a carbon atom as a function of the scattering angle (after M. M. Woolfson, 1970, *X–Ray Crystallography*, Cambridge University Press).

To proceed further with the evaluation of f_a, we need to know the electron density $\rho(\mathbf{r})$ for the atom in question. For this information we have to turn to the literature on atomic physics. Figure A.2b shows the scattering factor for carbon. There is one special direction for which f_a can be evaluated at once, namely the forward direction. In this case, $\theta = 0, s = 0$, and hence the oscillating factor $(\sin sr)/sr$ reduces to unity. Equation (A.10) then becomes

$$f_a = \int_0^R 4\pi r^2 \rho(r) dr,$$

and the integral is simply equal to the total number of electrons in the atom, i.e., the atomic number Z. We may therefore write

$$f_a(\theta = 0) = Z. \tag{A.11}$$

Thus for carbon $f_a(\theta = 0) = 6$ in agreement with Fig A.2b. The physical interpretation of eq. (A.11) is quite apparent: When one looks in the forward direction all the partial rays are in phase, and hence they interfere constructively.

2 Scattering from an crystal

Our primary aim in this chapter is, of course, to investigate the scattering from a crystal, and we shall no proceed to apply Eq. (A.8) to this situation. By analogy with the atomic, we define the *crystal scattering factor* f_{cr} as

$$f_{cr} = \sum_l e^{i\mathbf{s}\cdot\mathbf{r}_l}, \tag{A.12}$$

where the sum here extends over all the electrons in the crystal. To make use of the atomic scattering factor discussed in the previous section, we may split the sum (A.12) into two parts: First we sum over all the electrons in a single atom, and then sum all the atoms in the lattice. The double summation the amounts to the sum over all the electrons in the crystal, as required by (A.12). Since the first of the above sums leads to the atomic scattering factor, eq. (A.12) may thus be written in the form

$$f_{cr} = \sum_l f_{al} e^{i\mathbf{s}\cdot\mathbf{R}_l}, \tag{A.13}$$

where $\mathbf{R}_l$ is the position of the l th atom, and f_{al} the corresponding atomic factor.

It is now convenient to rewrite eq. (A.13) as a product of two factors, one involving a sum over the unit cell, and the other the sum over all unit cells in the crystal. Thus we define the *geometrical structure factor* F as

$$F = \sum_j f_{aj} e^{i\mathbf{s}\cdot\delta_j}, \tag{A.14}$$

where the summation is over all the atoms in the unit cell, and $\delta_\mathbf{j}$ is the relative position of the j th atom. Similarly we define the *lattice structure factor* as

$$S = \sum_l e^{i\mathbf{s}\cdot\mathbf{R}_l^{(c)}}, \tag{A.15}$$

where the sum extends over all the unit cells in the crystal, and $\mathbf{R}_l^{(c)}$ is the position of the l th cell. To express f_{cr} in terms of F and S, we return to eq. (A.13), write $\mathbf{R}_l = \mathbf{R}_l^{(c)} + \delta_j$, and then use eq. (A.14) and (A.15). The result is evidently

$$f_{cr} = FS. \tag{A.16}$$

Note that the lattice factor S depends only on the crystal system involved, while F depends on the geometrical shape as well as the contents of the unit cell. In the special

case of a simple lattice, where the unit cell contains a single atom, the factor F becomes equal to f_a. The factorisation of f_{cr} as shown in eq. (A.16) merits some emphasis: We have separated the purely structural properties of the lattice, which are contained in S, from the atomic properties contained in F. Great simplification is achieved thereby, because the two factors may now be treated independently. Since the factor F involves a sum over only a few atomic factors, it can be easily evaluated in terms of the atomic factors, as discussed in the previous section. We shall therefore not concern ourselves with this straightforward task for the moment, but press on and consider the evaluation of the lattice factor S.

The lattice structure factor The lattice structure factor S, defined in eq. (A.15), is of vital importance in the discussion of x–ray scattering. Let us now investigate its dependence on the scattering vector $\mathbf{s}$, and show that the values of $\mathbf{s}$ for which S does not vanish form a discrete set, which is found to be related to Bragg's law.

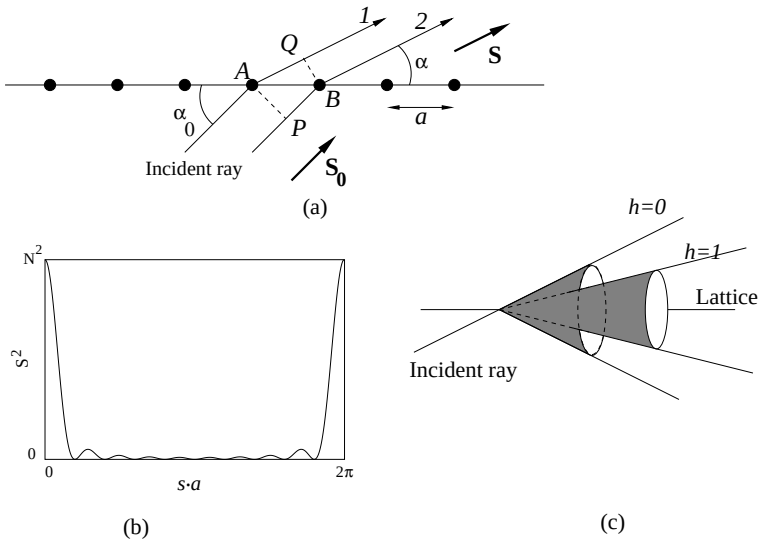

Figure A.3: (a) Scattering from a one–dimensional lattice. (b) Diffraction maxima. (c) Diffraction cones for first order ($h = 0$) and second order ($h = 1$) maxima.

We start with the simplest possible situation, an x–ray beam scattered from a one–dimensional monatomic lattice, as illustrated in Fig. A.3a. When we denote the basis vector of the lattice by $\mathbf{a}$, the structure factor becomes

$$S = \sum_{l=1}^{N} e^{i\mathbf{s}\cdot l\mathbf{a}}, \tag{A.17}$$

where we have substituted $\mathbf{R}_l^{(\mathbf{c})} = l\mathbf{a}$, and N is the total number of atoms. The series in eq. (A.17) is a geometric progression, the common ratio being $e^{i\mathbf{s}\cdot\mathbf{a}}$, and can readily be evaluated. The result is

$$S = \frac{\sin\left[\frac{1}{2}N\mathbf{s}\cdot\mathbf{a}\right]}{\sin\left[\frac{1}{2}\mathbf{s}\cdot\mathbf{a}\right]} \; \frac{e^{\frac{1}{2}iN\mathbf{s}\cdot\mathbf{a}}}{e^{\frac{1}{2}i\mathbf{s}\cdot\mathbf{a}}}$$

Physically, it is more meaningful to examine S^2 than S, since this is the quantity which

enters directly into calculations of intensity. It is given by

$$S^2 = \frac{\sin^2\left[\frac{1}{2}N\mathbf{s}\cdot\mathbf{a}\right]}{\sin^2\left[\frac{1}{2}\mathbf{s}\cdot\mathbf{a}\right]} \tag{A.18}$$

We now wish to see how this function depends on the scattering vector **s**. As we see from eq. (A.18), S^2 is the ratio of two oscillating functions having a common period $\mathbf{s}\cdot\mathbf{a} = 2\pi$, but, because N is much larger than unity in any practical case, the numerator oscillates far more rapidly than the denominator. Note, however, that for the particular value $\mathbf{s}\cdot\mathbf{a} = 0$, both the numerator and denominator vanish simultaneously, but the limiting value of S^2 is equal to N^2, a very large number. Similarly the value of S^2 at $\mathbf{s}\cdot\mathbf{a} = 2\pi$ is equal to N^2, as follows from the periodicity of S^2, as mentioned above. The function S^2 is sketched versus $\mathbf{s}\cdot\mathbf{a}$ in Fig. A.3b, for the range $0\langle\mathbf{s}\cdot\mathbf{a}\rangle 2\pi$. It has two primary maxima, at $\mathbf{s}\cdot\mathbf{a} = 0$ and $\mathbf{s}\cdot\mathbf{a} = 2\pi$, separated by a large number of intervening subsidiary maxima, the latter resulting from the rapid oscillations of the numerator in eq. (A.18). Calculations show that when the number of cells is very large, as it is in actual cases, the subsidiary maxima are negligible compared with the primary ones. For instance, the peak of the highest subsidiary maximum is only 0.04 that of a primary maximum. It is therefore a good approximation to ignore all the subsidiary maxima, and take the function S^2 to be a nonvanishing only in the immediate neighbourhoods of the primary maxima. Furthermore, it can also be demonstrated that the width of each primary maximum decreases rapidly as N increases, and that this width vanishes in the limit as $N \to \infty$. Therefore S^2 is nonvanishing only at the values given exactly by $\mathbf{s}\cdot\mathbf{a} = 0, 2\pi$. But because S^2 is periodic, with period of 2π, it is also finite at all the values

$$\mathbf{s}\cdot\mathbf{a} = 2\pi h, \quad h = \text{any integer}. \tag{A.19}$$

At these values S^2 is equal to N^2, and hence $S = N$.

Equation (A.18) determines all the directions in which S has a nonzero value and hence the directions in which diffraction takes place. The physical interpretation of this equation is straightforward. Recalling the definition of **s**, Eq. (A.4), and referring to Fig A.3, we obtain

$$\mathbf{s}\cdot\mathbf{a} = \frac{2\pi}{\lambda}(S - S_0)\cdot\mathbf{a} = \frac{2\pi}{\lambda}(AQ - PB),$$

which is the phase difference between the two consecutive scattered rays. Thus Eq. (A.19) is the condition for constructive interference, i.e., the lattice scattering factor survives only in these directions, which is hardly surprising.

For a given h, the condition Eq. (A.19) does not actually determine a single direction, but rather an infinite number of directions forming a cone whose axis lies along the lattice line. To see this, we can write Eq. (A.19) as

$$\frac{2\pi}{\lambda}(\cos\alpha - \cos\alpha_0) = 2\pi h, \tag{A.20}$$

where α_0 is the angle between the incident beam and the lattice line and α is the corresponding angle for the diffracted beam. Thus for a given h and α_0, the beam diffracts along all directions for which α satisfies Eq. (A.20). These form a cone whose axis lies along the lattice , and whose half angle is equal to α. The case $h = 0$ is a special one;

its cone includes the direction of forward scattering. Diffraction cones corresponding to several values of h are shown in Fig. A.3c.

In treating the lattice structure factor, we have so far confined ourselves to the case of a one–dimensional lattice. Referring to Eq. (A.15) and substituting for the lattice vector,

$$\mathbf{R}^{(c)} = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c},$$

where $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ are the basis vectors, we find for the structure factor

$$S = \sum_{l_1,l_2,l_3} e^{i\mathbf{s}\cdot(l_1\mathbf{a}+l_2\mathbf{b}+l_3\mathbf{c})},$$

where the triple summation extends over all the unit cells in the crystal. We can separate this sum into three partial sums,

$$S = \left(\sum_{l_1} e^{i\mathbf{s}\cdot l_1\mathbf{a}}\right)\left(\sum_{l_2} e^{i\mathbf{s}\cdot l_2\mathbf{b}}\right)\left(\sum_{l_3} e^{i\mathbf{s}\cdot l_3\mathbf{c}}\right),$$

and in this manner we factor out S into a product of one–dimensional factors, and we can therefore use the result we developed earlier. The condition for constructive interference is that each of the three factors must be finite individually, and this means that $\mathbf{s}$ must satisfy the following three equations simultaneously:

$$\begin{aligned} \mathbf{s}\cdot\mathbf{a} &= h2\pi \\ \mathbf{s}\cdot\mathbf{b} &= k2\pi \\ \mathbf{s}\cdot\mathbf{c} &= l2\pi \end{aligned} \tag{A.21}$$

where h, k, and l are any set of integers. Written in terms of the angles made by $\mathbf{s}$ with the basis vectors, in analogy with Eq. (A.19), these equations become respectively

$$\begin{aligned} a\,(\cos\alpha - \cos\alpha_0) &= h\lambda \\ b\,(\cos\beta - \cos\beta_0) &= k\lambda \\ c\,(\cos\gamma - \cos\gamma_0) &= l\lambda \end{aligned} \tag{A.22}$$

where α_0, β_0, and γ_0 are the angles which the incident beam makes with the basis vectors, while α, β, and γ are the corresponding angles for the diffracted beam. Equations (A.21) and (A.22) are known as the *Laue equations*, after the physicist who first derived them.

The question is how to determine the values of the scattering vector $\mathbf{s}$ which satisfy the diffraction condition Eq. (A.21). We shall show in the next section that these values form a discrete set which corresponds to Bragg's law.

3 The reciprocal lattice and X–ray diffraction

Starting with a lattice whose basis vectors are $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, we can define a new set of basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ according to the relations

$$\mathbf{a}^* = \frac{2\pi}{\Omega_c}\,(\mathbf{b}\ \mathbf{x}\ \mathbf{c})\,,\ \mathbf{b}^* = \frac{2\pi}{\Omega_c}\,(\mathbf{c}\ \mathbf{x}\ \mathbf{a})\,,\ \mathbf{c}^* = \frac{2\pi}{\Omega_c}\,(\mathbf{a}\ \mathbf{x}\ \mathbf{b})\,, \tag{A.23}$$

where $\Omega_c = \mathbf{a} \cdot (\mathbf{bxc})$, the volume of a unit cell. We can now use the vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ as a basis for a new lattice whose vectors are given by

$$\mathbf{G_n} = n_1\mathbf{a}^* + n_2\mathbf{b}^* + n_3\mathbf{c}^*, \tag{A.24}$$

where n_1, n_2, and n_3 are any set of integers. The lattice we have just defined is known as the *reciprocal lattice*, and $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are called the *reciprocal basis vectors*. [3]

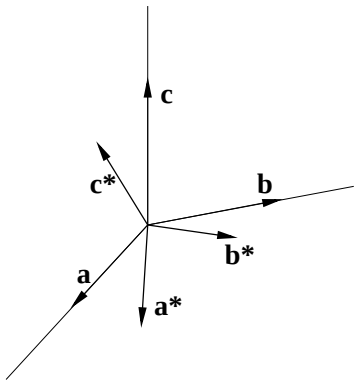

Figure A.4: Reciprocal basis vectors

The relation of the reciprocal basis vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ to the direct basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ is shown in Fig A.4. The vector $\mathbf{a}^*$, for instance , is normal to the plane defined by the vectors $\mathbf{b}$ and $\mathbf{c}$, and analogous statements apply to $\mathbf{b}^*$ and $\mathbf{c}^*$. Also note that if the direct basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ form an orthogonal set, then $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ also form another orthogonal set $\mathbf{a}^*$ parallel to $\mathbf{a}$, $\mathbf{b}^*$ parallel to $\mathbf{b}$, and $\mathbf{c}^*$ parallel to $\mathbf{c}$ In general, of course, neither set is orthogonal.

The following mathematical relations are useful in dealing with the reciprocal lattice:

$$\mathbf{a}^* \cdot \mathbf{a} = 2\pi, \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = 0, \mathbf{b}^* \cdot \mathbf{b} = 2\pi, \mathbf{b}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{c} = 0, \mathbf{c}^* \cdot \mathbf{c} = 2\pi, \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = 0.$$

The first row of equations, for instance, can be established as follows: To prove the first of the equations, we substitute for $\mathbf{a}^*$ from eq. (A.23) and find that

$$\mathbf{a}^* \cdot \mathbf{a} = \frac{2\pi}{\Omega_c} (\mathbf{b \ x \ c}) \cdot \mathbf{a}.$$

But $(\mathbf{b \ x \ c}) \cdot \mathbf{a}$ is also equal to the volume of the unit cell Ω_c, and hence $\mathbf{a}^* \cdot \mathbf{a} = 2\pi$, as required. The second two equations in the first row reflect the fact, already mentioned, that $\mathbf{a}^*$ is perpendicular to the plane formed by $\mathbf{b}$ and $\mathbf{c}$. The remainder of the equation in Eq. (A.25) can be established in a similar manner.

Examples of the reciprocal lattices are shown in Fig. A.5. Figure A.5a shows a direct one–dimensional lattice and its reciprocal. Note that in this case $\mathbf{a}^*$ is parallel to $\mathbf{a}$, and that $\mid \mathbf{a}^* \mid = 2\pi/a$. Figure A.5b shows a plane rectangular lattice and its reciprocal. [4]

[3] For the construction of the reciprocal lattice to be valid, the real basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ must form a primitive basis; in other words, the cell in the real lattice must be primitive.

[4] In one and two dimensions, Eq. (A.23), which defines the reciprocal lattice, does not apply because the vector cross product is defined only in three dimensions. Therefore in dealing with one– and two–dimensional lattices, we use instead Eq. (A.25) to define the reciprocal lattice.

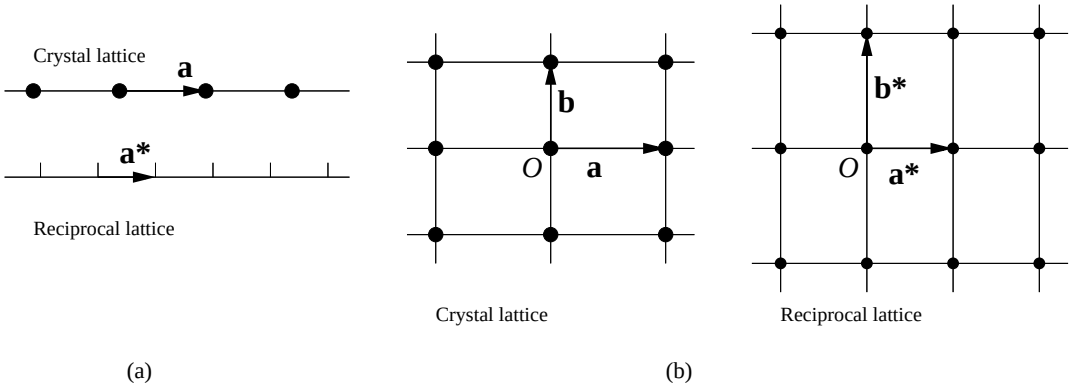

Figure A.5: (a) Reciprocal lattice for a one–dimensional crystal lattice. (b) Reciprocal lattice for a two–dimensional lattice.

Three–dimensional examples are more complex, but the procedure for finding them is straightforward. One employs Eq. (A.23) to find the basis $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ and the uses Eq. (A.24) to locate all the lattice points. It is evident, for instance, that the reciprocal of an sc lattice of edge a is also an sc lattice with a cube edge equal to $2\pi/a$ (Fig. A.6).

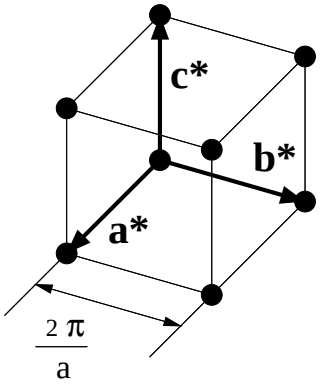

Figure A.6: A part of the reciprocal lattice for an sc lattice.

We can similarly establish that the reciprocal of a bcc is an fcc lattice, and vice versa (See Kittel chapter 2). One may extend the argument to other crystal systems. When we realise that the reciprocal lattice is a lattice in its own right, and that it possesses the same rotational symmetry as the direct lattice, we see that the the reciprocal lattice always falls in the same crystal system as its direct lattice (see Kittel table 1 and figure 10 on pages 10–11). Thus the reciprocal for monoclinic, triclinic,... and hexagonal lattices are also monoclinic, triclinic,... and hexagonal, respectively. (Note, however, that the two lattices need not have the same Bravais structure within the same system; see the bcc and fcc examples above.)

The unit cell of the reciprocal is chosen in particular manner. For the rectangular lattice of Fig A.7, let O be the origin point, and draw the various lattice vectors connecting the with the neighbouring lattice points. Then draw the straight lines which are perpendicular to these vectors at their midpoints. The smallest area enclosed by these lines, the rectangle A in the figure, is the unit cell we are seeking, and is called the *first Brillouin zone*. This Brillouin zone (BZ) is an acceptable unit cell because it satisfies all the necessary requirements. It also has the property that its corresponding lattice point

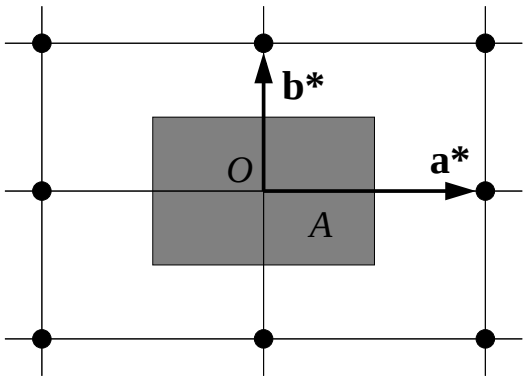

Figure A.7: The first Brillouin zone for a rectangular lattice.

falls precisely at the center, unlike the case of the direct lattice, in which the lattice points usually lie at the corners of the cell. If the first BZ is now translated by all the reciprocal vectors $\mathbf{G_n}$, then the whole reciprocal lattice space is covered, as it must be, since the BZ is a true unit cell.

The Brillouin zone for a 3–dimensional lattice can be constructed in a similar manner, but note that in this case the lattice vectors are bisected by perpendicular planes, and that the first BZ is now the smallest *volume* enclosed by these planes. In the simplest case, the sc lattice, the BZ is a cube of edge $2\pi/a$, centered at the origin. The BZ's for the other cubic lattices are more complicated in shape, and we shall defer discussion of these and other lattices to a later section (See Kittel chapter 2).

Sometimes one also uses higher–order Brillouin zones, which correspond to vectors joining the origin to farther points in the reciprocal lattice, but we shall not discuss these here, as they will not be needed. We shall find that the concept of the Brillouin zone is very important in connection with lattice vibrations, and electron states in a crystal (See Kittel chapter 4, 5 and 7).

Having defined the reciprocal lattice and discussed some of its properties, let us now proceed to demonstrate its usefulness. One important application lies in its use in the evaluation of lattice sums, and this rests on the following mathematical statement:

$$\sum_{i=1}^{N} e^{i\mathbf{A}\cdot\mathbf{R_l}} = N\delta_{\mathbf{A},\mathbf{G_n}}. \tag{A.25}$$

Here $\mathbf{A}$ is an arbitrary vector, the summation is over the direct lattice vectors, footnote and N is the total number of cells in the direct lattice. Because of the delta symbol, the meaning of Eq. (A.25) is that the lattice sum on the left vanishes whenever the vector $\mathbf{A}$ is not equal to some reciprocal lattice vector $\mathbf{G_n}$. When this is equal to some $\mathbf{G_n}$, however, the lattice sum becomes equal to N. To establish the validity of Eq. (A.25), we shall first treat the case $\mathbf{A} = \mathbf{G_n}$; to evaluate the exponent $\mathbf{A}\cdot\mathbf{R_l}$ on the left of Eq. (A.25), we substitute $\mathbf{A} = \mathbf{G_n} = n_1\mathbf{a}^* + n_2\mathbf{b}^* + n_3\mathbf{c}^*$ and $\mathbf{R_l} = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c}$, and the result is

$$\mathbf{A}\cdot\mathbf{R_l} = \mathbf{G_n}\cdot\mathbf{R_l} = (n_1\mathbf{a}^* + n_2\mathbf{b}^* + n_3\mathbf{c}^*)\cdot(l_1\mathbf{a_1} + l_2\mathbf{a_2} + l_3\mathbf{a_3}) = (n_1l_1 + n_2l_2 + n_3l_3)\,2\pi,$$

where in evaluating the scalar products of the basis vectors we used Eq. (A.25). For example, $\mathbf{a}^*\cdot\mathbf{a} = 2\pi, \mathbf{a}^*\cdot\mathbf{b} = \mathbf{0}$, etc. Each term in the sum in Eq. (A.25) is therefore of

the form $e^{im2\pi}$, where m is an integer and is consequently equal to unity. The total sum is then equal to N, as demanded by Eq. (A.25). In the case $\mathbf{A} \neq \mathbf{G_n}$, we can follow the same procedure employed in evaluating Eq. (A.17), and the result is the same as before, namely, that for large N the sum vanishes except for certain values of $\mathbf{A}$. The exceptional values are, in fact, those singled out above, that is, $\mathbf{A} = \mathbf{G_n}$.

As a final point, we shall now show that the vectors of the reciprocal lattice are related to the crystal planes of the direct lattice. In this manner, the somewhat abstract reciprocal vectors will acquire a concrete meaning. Consider the set of crystal planes whose Miller indices are (hkl) and the corresponding reciprocal lattice vector $\mathbf{G_{hkl}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, where the numbers h, k, and l are a set of integers. We shall now establish the following properties:

1 The vector $\mathbf{G_{hkl}}$ is normal to the (hkl) crystal planes.

2 The inter planar distance d_{hkl} is related to the magnitude of $\mathbf{G_{hkl}}$ by

$$d_{hkl} = 2\pi/G_{hkl}. \tag{A.26}$$

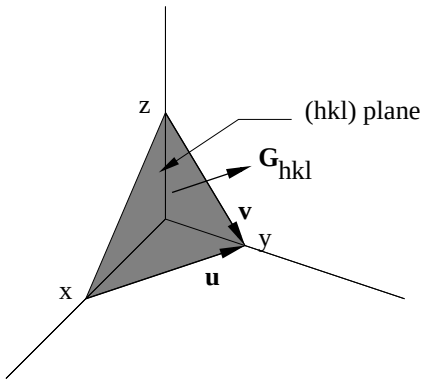

Figure A.8: The reciprocal lattice vector $\mathbf{G_{hkl}}$ is normal to the plane (hkl).

To establish these relations, we refer to Fig. A.8, where we have drawn one of the (hkl) planes. The intercepts of the plane with the axes are x, y, z and they are related to the indices by

$$(h, k, l) \sim \left(\frac{1}{x}, \frac{1}{y}, \frac{1}{z}\right), \tag{A.27}$$

where use is made of the definition of the Miller indices (See Kittel page 12). Note also the vectors $\mathbf{u}$ and $\mathbf{v}$ which lie along the lines of intercepts of the plane with the xy and yz planes, respectively. According to the figure, these vectors are given by $\mathbf{u} = x\mathbf{a} - y\mathbf{b}$, and $\mathbf{v} = y\mathbf{b} - z\mathbf{c}$. In order to prove relation (1) above, we need only prove that $\mathbf{G_{hkl}}$ is orthogonal to both $\mathbf{u}$ and $\mathbf{v}$. We have

$$\mathbf{u} \cdot \mathbf{G_{hkl}} = (x\mathbf{a} - y\mathbf{b}) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) = 2\pi\,(xh - yk) = 0 \tag{A.28}$$

where we have used Eq. (A.25) to establish the second equality; the last equality follows from Eq. (A.27). In the same manner we can also show that $\mathbf{G_{hkl}}$ is orthogonal to $\mathbf{v}$, and this establishes property (1).

In order to prove Eq. (A.26), one observes that d_{hkl}, the inter planar distance, is equal to the projection of $x\mathbf{a}$ along the direction normal to the (hkl) planes; this direction can be represented by the unit vector $\hat{\mathbf{G}}_{\mathbf{hkl}} = \mathbf{G}_{\mathbf{hkl}}/G_{hkl}$, since we have already established that $\mathbf{G}_{\mathbf{hkl}}$ is normal to the plane. Therefore

$$d_{hkl} = x\mathbf{a} \cdot \hat{\mathbf{G}}_{\mathbf{hkl}} = (x\mathbf{a} \cdot \mathbf{G}_{\mathbf{hkl}}) / G_{hkl}.,$$

We now note that $x\mathbf{a} \cdot \mathbf{G}_{\mathbf{hkl}} = 2\pi hx$, and this is equal to 2π, because, according to Eq. (A.27), $xh = 1$. This completes the proof of Eq. (A.26).

The connection between reciprocal vectors and crystal planes is now quite clear. The vector $\mathbf{G}_{\mathbf{hkl}}$ is associated with the crystal planes (hkl), which are, in fact, normal to it, and the separation of these planes is 2π times the inverse of the length G_{hkl} in the reciprocal space. The crystallographer prefers to think in terms of the crystal planes, which have a physical reality, and their Miller indices, while the solid–state physicist prefers the reciprocal lattice, which is mathematically more elegant; the two approaches are, however, equivalent, and one can change from one to the other by using the relations connecting the two. Of the two approaches, we shall mostly use the reciprocal lattice in this book.

4 The diffraction condition and Bragg's law

We shall now employ the concept of the reciprocal lattice to evaluate the lattice–structure factor S, which is involved in the x–ray scattering process. This factor is given in Eq. (A.15). Comparing this with Eq. (A.25), we see that S vanishes for every value of $\mathbf{s}$ except where

$$\mathbf{s} = \mathbf{G}_{\mathbf{hkl}}. \tag{A.29}$$

The condition for diffraction is therefore that the scattering vector $\mathbf{s}$ is equal to a reciprocal lattice vector. Equation (A.29) implies that $\mathbf{s}$ is normal to the (hkl) crystal planes [property (1) above], as shown in Fig. A.9. The equation can be rewritten in a different form. Recalling that $s = 2(2\pi/\lambda)\sin\theta, G_{hkl} = 2\pi/d_{hkl}$, and substituting into Eq. (A.29), we find that

$$2d_{hkl}\sin\theta = \lambda. \tag{A.30}$$

This is exactly the same form as Bragg's law ($2d\sin\theta = n\lambda$), which is seen to follow from the general treatment of scattering theory. It is therefore physically meaningful to use the Bragg model, and speak of reflection from atomic planes. This manner of viewing the diffraction process is conceptually simpler than that of scattering theory.

When the condition (A.29) is satisfied, the structure factor is nonzero, and its value is equal to N as seen from Eq. (A.25). Thus

$$S_{hkl} = N.$$

Substituting this into Eq. (A.23), we find the crystal scattering factor f_{cr} to be

$$f_{cr,hkl} = NF_{hkl},$$

and the intensity I is then

$$I \sim \mid f_{cr,hkl} \mid^2 \sim \mid F_{hkl} \mid^2 . \tag{A.31}$$

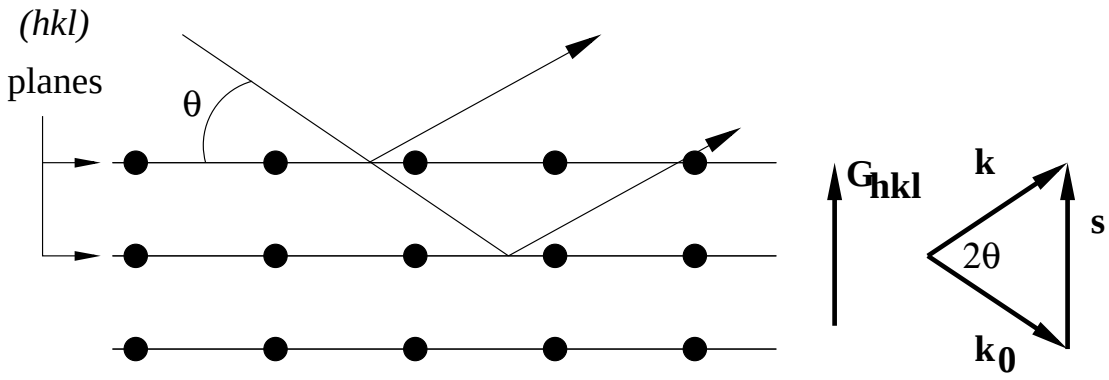

Figure A.9: The scattering vector is equal to a reciprocal lattice vector.

The scattered intensity vanishes in all directions except those in which the structure factor S is nonvanishing. These latter directions are therefore the directions of diffraction: they are the ones which satisfy the condition of constructive interference. When the Bragg condition is satisfied, then the incident beam is diffracted into a single beam (neglecting higher orders), which is recorded at the detector as a single spot on the film. This spot represents the whole set of reflecting planes (hkl). When the crystal is rotated so that the a new set of planes again satisfies the Bragg condition, then this new set appears as a new spot on the film at the detector. Therefore each spot on the film represents a whole set of crystalline planes, and from the arrangement of these spots one can determine the structure of the crystal, as discussed in the lab–instruction.

According to our statements, each diffracted beam can be associated with a set of planes of certain Miller indices; this is evident from Eq. (A.31). It is experimentally observed, however, that diffraction from certain planes may be missing. This is due to the geometrical structure factor F_{hkl}, which depends on the shape and contents of the unit cell. Thus, if F_{hkl} is zero for certain indices, then the intensity vanishes according to Eq. (A.31), even though the corresponding planes satisfy the Bragg condition. To evaluate F_{hkl}, we return to Eq. (A.14). We assume the atoms to be identical, and take $\delta_{\mathbf{j}} = \mathbf{u_j a} + \mathbf{v_j b} + \mathbf{w_j c}$, where $\delta_{\mathbf{j}}$ is the position of the jth atom. Furthermore, we take

$$\mathbf{s} = \mathbf{G_{hkl}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \tag{A.32}$$

Therefore

$$F_{hkl} = f_a \sum_j e^{i2\pi(hu_j + kv_j + lw_j)}. \tag{A.33}$$

Consider, for instance, the bcc lattice. The unit cell has two atoms whose coordinates are $(u_j, v_j, w_j) = (0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Using Eq. (A.33), one has

$$F_{hkl} = f_a \left(1 + e^{i\pi(h+k+l)}\right) .. \tag{A.34}$$

This expression can take only two values; when $(h + k + l)$ is even, $F_{hkl} = 2f_a$, while $F_{hkl} = 0$ when $(h + k + l)$ is odd. Thus for the bcc lattice, the diffraction is absent for all those planes in which the sum $(h + k + l)$ is odd, and is present for the planes in which $(h + k + l)$ is even. We have it as a problem to show that in an fcc lattice the allowed reflections correspond to the cases in which h, k, l are either all even or all odd. Note

that the missing planes give direct information concerning the symmetry of the unit cell. footnote

Equation (A.29) can be rewritten in still another form. We recall from Eq. (A.4a) that $\mathbf{s} = \mathbf{k} - \mathbf{k_0}$, where $\mathbf{k_0}$ and $\mathbf{k}$ are the vectors of incident and diffracted beams. Substituting into (A.29), one finds

$$\mathbf{k} = \mathbf{k_0} + \mathbf{G}.$$

Multiplication of both sides by $\hbar$ leads to

$$\hbar\mathbf{k} = \hbar\mathbf{k_0} + \hbar\mathbf{G}.$$

But the quantity $\hbar\mathbf{k}$ is the momentum of the x–ray photon associated with the beam (see the de Broglie relation). Thus the above equation may be viewed as momentum conservation, and the diffraction process as a collision process between the x–ray photon and the crystal. In the collision the photon recoils and gains a momentum $\hbar\mathbf{G}$. Conversely, the crystal recoils in the opposite direction with a momentum $-\hbar\mathbf{G}$. The recoil energy of the crystal is very small because the motion is that of a rigid–body displacement, and therefore the kinetic energy is $(\hbar G)^2/2M$, where M is the total mass of the crystal. Since M is extremely large compared with the mass of the atom, the recoil energy is very small, and may be neglected. Therefore the collision process may be regarded as elastic; this has benn implicitly assumed throughout, of course, since we have taken k to be equal to k_0.

B

Problems in Solid State Physics

1 Crystal Structures

1.1. Given that the primitive basis vectors of a lattice are

$$\begin{aligned} \mathbf{a} &= (a/2)(\hat{x} + \hat{y}), \\ \mathbf{b} &= (a/2)(\hat{y} + \hat{z}), \\ \mathbf{c} &= (a/2)(\hat{z} + \hat{x}), \end{aligned} \tag{B.1}$$

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors in the x-, y- and z-directions of a Cartesian coordinate system.

(a) Determine the Bravais lattice.

(b) Calculate the volume of the primitive unit cell.

1.2. The angles between the tetrahedral bonds of diamond are the same as the larger angle between two body diagonals of a cube. Use elementary vector analysis to find the value of the angle.

1.3. Use information about the structure and the atomic weights to calculate the densities of the following solids: Al, Fe, Zn and Si.

1.4. Show that in an ideal hexagonal close-packed (hcp) structure, where the atomic spheres touch each other, the ratio c/a is given by

$$\frac{c}{a} = \left(\frac{8}{3}\right)^{1/2} = 1.633. \tag{B.2}$$

1.5. The packing ratio is defined as the fraction of the total volume of the cell that is filled by atoms. Determine the maximum values of this ratio for equal spheres located at the points of SC, BCC, FCC and diamond type crystals.

1.6. Draw an FCC cubic cell. Construct a primitive cell within this larger cell, and compare the two. How many atoms are in the primitive cell and how does this compare with the number in the cubic cell.

1.7. Show that a two-dimensional lattice may not possess a 5-fold rotational symmetry.

1.8. Demonstrate the fact that if an object has two reflection planes intersecting at $\pi/4$ it also possesses a 4-fold axis lying at their intersection.

1.9. Determine which planes in an FCC structure have the highest density of atoms and evaluate this density for Cu.

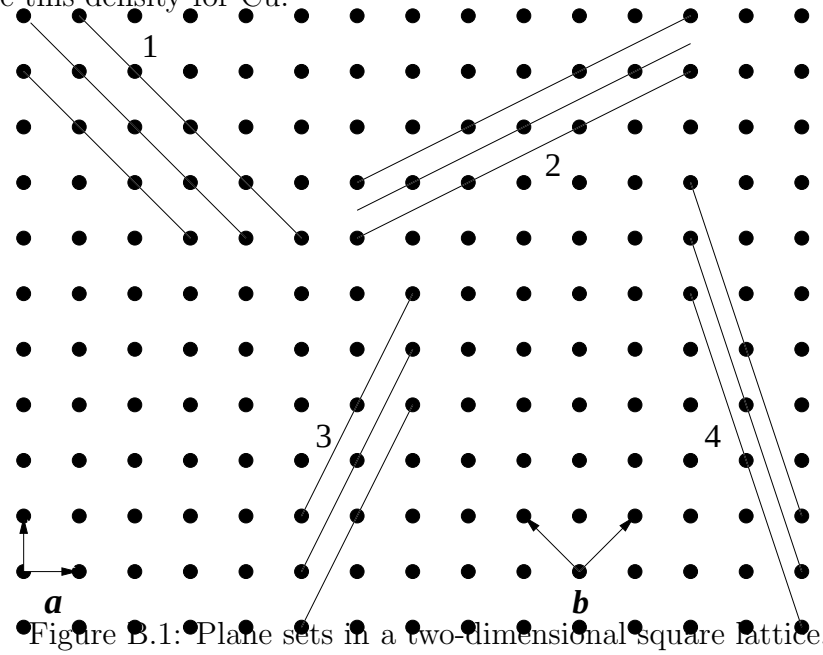

Figure B.1: Plane sets in a two-dimensional square lattice.

1.10. Determine the Miller indices of the four sets of planes in Fig.B.1. Do this in the two coordinate systems a and b.

2 The Reciprocal Lattice

2.1. Show that the reciprocal lattice to the reciprocal lattice is the real lattice.

2.2. (a) Calculate the primitive translation vectors of the reciprocal lattice for a simple cubic (SC) lattice with the cube edge a and determine the Bravais lattice of the reciprocal lattice.

(b) Do the same thing for a BCC lattice with the cube edge a.

(c) Do the same thing for an FCC lattice with the cube edge a.

2.3. A reciprocal lattice vector has a dimension equal to the reciprocal of length. Is it meaningful to compare the magnitudes of a direct-lattice vector $\mathbf{R}$ with reciprocal lattice vector $\mathbf{G}$? Is it meaningful to compare their directions? If the answer is yes, find the angle between $\mathbf{R}$ and $\mathbf{G}$ in terms of their components in a cubic crystal. $\mathbf{R} = [111]$ and $\mathbf{G} = [110]$.

2.4. Does a real lattice vector have a corresponding unique reciprocal vector?

2.5. Show that the volume of the primitive reciprocal cell is $\Omega = (2\pi)^3/V$, where V is the volume of the corresponding cell in real space. Recall the vector identity $(\mathbf{C} \times \mathbf{A}) \times (\mathbf{A} \times \mathbf{B}) = (\mathbf{C} \cdot \mathbf{A} \times \mathbf{B})\mathbf{A}$.

2.6. Calculate the volume of the Brillouin zone for Na and Au.

2.7. Draw the first, second and third Brillouin zones of a square lattice. Show that the area of the second and third zone is equal to that of the first. Do this by appropriately displacing the various fragments until the first zone is covered completely.

2.8. Draw the first two zones for a two-dimensional rectangular lattice for which the ratio of the lattice vectors $a/b = 2$. Show that the areas of the zones are equal.

2.9. Show that the reciprocal lattice for a two-dimensional hexagonal lattice with $|\mathbf{a}_1| = |\mathbf{a}_2| = a$ and $\beta = 60^\circ$ also is a hexagonal lattice. The reciprocal lattice is rotated compared with the real lattice. How large is this rotation? What is the lattice constant of the reciprocal lattice?

2.10. Construct the reciprocal lattice for a two-dimensional lattice in which $|\mathbf{a}_1| = 1.25$, $|\mathbf{a}_2| = 2.50$ and $\beta = 120^\circ$.

2.11. Calculate the shortest distance from the origin in k-space to the first Brillouin zone boundary for Li and Ag.

3 Diffraction in Crystals

3.1. What is the justification for drawing the scattered rays as nearly parallel?

3.2. What is the justification for assuming elastic scattering of X-rays when they are scattered by a crystal?

3.3. The amplitude of a scattered wave decreases as the inverse of the radial distance from the scattering center. Justify this on the basis of energy conservation.

3.4. The scattering amplitude is a complex number. What is the advantage of using complex representation?

3.5. Diamond and silicon have the same type of lattice structure, an FCC with a basis. Is the lattice structure factor the same for both substances?

3.6. Why is the energy of a neutron so much smaller than that of an electron in radiation beams employed in crystal diffraction?

3.7. Can a light beam be used in the analysis of crystal structure?

3.8. Why is the neutron more useful than the proton in structure analysis?

3.9. The minimum wavelength observed in X-ray radiation is 1.23 Å. What is the kinetic energy of the primary electrons hitting the target?

3.10. The edge of a unit cell in a simple cubic crystal is a = 2.62 Å. Find the Bragg angle corresponding to reflection from the planes (100), (110), (200), (210) and (211), given that the monochromatic X-ray has a wavelength of 1.54 Å.

3.11. A Cu target emits an X-ray of wavelength 1.54 Å.

(a) Given that the Bragg angle for reflection from the (111)-planes in Al is 19.2°, compute the inter planar distance for these planes.

(b) Knowing that the density and atomic weight are, respectively, 2700 kg/m^3 and 27.0 kg/kmol, compute Avogadro's number.

3.12. The Bragg angle for reflection from the (110)-planes in BCC iron is 22° for an X-ray wavelength of 1.54 Å

(a) Calculate the cube length.

(b) What is the Bragg angle for reflection from the (111)-planes?

(c) Calculate the density of BCC iron. The atomic weight is 55.8 kg/kmol.

3.13. The electron density in an hydrogen atom in its ground state is spherically symmetric and given by

$$n(r) = \frac{e^{-2r/a_0}}{\pi a_0^3} \tag{B.3}$$

where a_0, the first Bohr radius, has the value 0.53 Å. Show that the atomic form factor is $f_G = 16/(4 + G^2 a_0^2)^2$.

3.14. The scattered intensity for a linear crystal is given by the expression

$$I = \frac{\sin^2 \frac{1}{2} M(a \cdot \Delta k)}{\sin^2 \frac{1}{2}(a \cdot \Delta k)}, \tag{B.4}$$

where M is the number of scattering centers and a the lattice constant. Evaluate the first subsidiary maximum and show that it is equal to $0.045M^2$, in the limit of large M.

3.15. The structure factor of the basis of a BCC lattice may be evaluated by assuming the cell to contain one atom at a corner and another at the center of the unit cell. Show that the same result is obtained by taking the cell to contain one eighth of an atom at each of its eight corners, plus one atom at the center.

3.16. Which of the following reflections would be missing in a BCC lattice: (100), (110), (111), (200), (210), (220) and (211)? Answer a similar question for an FCC lattice.

3.17. Evaluate the structure factor of the basis for the diamond structure. Express it in terms of the corresponding factor for the FCC Bravais lattice. Show that the allowed reflections satisfy $h + k + l = 4n$, where all indices are even and n any integer; or else all indices are odd. Which of the reflections in problem 3.16 are allowed?

3.18. Cesium chloride (CsCl) crystallises in a cubic structure, in which one type of atom is located at the corners and the other at the center of the cell. Draw the cubic unit cell and calculate the structure factor of the basis assuming that $f_{Cs} = 3f_{Cl}$. Explain why the extinction rule for the BCC Bravais lattice is violated here.

3.19. Show that if a crystal undergoes volume expansion than the reflected beam is rotated by the angle

$$\delta\theta = -\frac{\delta V}{3V} \tan\theta. \tag{B.5}$$

3.20. A beam of 150 eV electrons falls on a powder nickel sample. Find the three smallest Bragg angles at which reflection takes place.

3.21. In an X-ray diffraction experiment on NaCl, diamond and CsCl the following results was determined:

Bragg angle	Sample A	Sample B	Sample C
θ_1	10.8°	13.7°	22.0°
θ_2	15.3°	15.9°	37.7°
θ_3	18.9°	22.8°	45.8°
θ_4	22.0°	27.0°	59.8°
θ_5	24.7°	28.3°	70.4°

Determine which sample is which?

4 Crystal Binding

4.1. What is the reason for the fact that the tetrahedral bond is the dominant bond in the diamond structure?

4.2. Estimate the strength of the bond between water molecules in electron volts per bond.

4.3. Show that two parallel electric dipoles attract each other.

4.4. Show that the van der Waals binding energy is $\sim 1/R^6$. Use two atoms and assume that they are linear harmonic oscillators separated by R and that each oscillator bears charges $\pm e$ with separations x_1 and x_2.

4.5. Estimate the strength of the van der Waals bond for neon in electron volts per bond.

4.6. A quantitative theory of bonding in ionic crystals was developed by Born and Meyer. The total potential energy of the system is taken to be

$$E = N\left(\frac{A}{R^n} - \frac{\alpha e^2}{4\pi\epsilon_o R}\right), \tag{B.6}$$

where N is the number of positive-negative ion pairs and α is the Madelung constant. A and n are constants determined from experiments.

(a) Show that the equilibrium inter atomic distance is given by the expression

$$R_0^{n-1} = \frac{4\pi\epsilon_o A}{\alpha e^2} n. \tag{B.7}$$

(b) Establish that the bonding energy at equilibrium is

$$E_0 = -\frac{\alpha N e^2}{4\pi\epsilon_o R_0}\left(1 - \frac{1}{n}\right). \tag{B.8}$$

(c) Calculate the constant n for NaCl, given that the measured binding energy for this crystal is 7.95 eV/molecule and $\alpha = 1.75$.

5 Lattice Vibrations

5.1. Plot the first three allowed vibrational modes in a continuous line under the boundary conditions $u(0) = u(L)$ and $u(0) = u(L) = 0$.

5.2. Determine the density of states for a two-dimensional continuous medium using periodic boundary conditions.

5.3. In the Einstein model, atoms are treated as independent oscillators. The Debye model, on the other hand, treats atoms as coupled oscillators vibrating collectively, but the collective modes are regarded as independent. Explain the meaning of this independence, and contrast it with that in the Einstein model.

5.4. Would you expect to find sound waves in small molecules? If not, how do explain the propagation of sound in gaseous substances?

5.5. Explain qualitatively why the inter atomic force constant diminishes rapidly with distance.

5.6. Determine the dispersion relation of phonons in a one-dimensional crystal with one atom per primitive cell. Also plot the relation.

5.7. The dispersion relation for a one-dimensional crystal with two atoms per cell is

$$\omega^4 - 2C\frac{M_1 + M_2}{M_1 M_2}\omega^2 + \frac{2C^2}{M_1 M_2}(1 - \cos Ka) = 0, \tag{B.9}$$

where a is the length of the cell and M_1, M_2 are the masses of the two atoms. Determine the roots to the dispersion relation at the Brillouin zone center and at the zone boundary. Also plot the relation.

5.8. Show that the total number of allowed modes in the first BZ of a one-dimensional diatomic lattice is equal to $2N$, the total number of degrees of freedom.

5.9. Suppose that we allow the two masses M_1 and M_2 in a one-dimensional diatomic lattice to become equal. What happens with the frequency gap?

5.10. Derive an expression for the specific heat of a one-dimensional diatomic lattice. Make the Debye approximation for the acoustic branch and assume that the optical branch is flat. Investigate the high- and low-temperature limits.

Hint:

$$\int_0^\infty \frac{x^2 e^x}{(e^x - 1)^2} dx = \frac{\pi^2}{3} \tag{B.10}$$

5.11. According to classical theory the average energy of an atom in a crystal is given by the expression

$$E_{Atom} = 3\frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left(\frac{p_x^2}{2m} + \frac{1}{2}kx^2\right)e^{-\left(\frac{p_x^2}{2m}+\frac{1}{2}kx^2\right)/k_BT}dp_x dx}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}e^{-\left(\frac{p_x^2}{2m}+\frac{1}{2}kx^2\right)/k_BT}dp_x dx} \tag{B.11}$$

Evaluation of this integral yields the value $E_{Atom} = 3k_BT$.

(a) Evaluate the heat capacity and compare with experimental data for Cu and diamond.

(b) Evaluate the atom energy for Cu at the Debye temperature according to the classical theory. The Debye temperature for Cu is 340 K.

(c) Evaluate the actual thermal energy according to the Debye theory and compare with the classical value obtained above. For the purpose of this calculation, you may approximate the Debye curve by a straight line joining the origin to the point on the Debye curve at $T = \theta_D$.

5.12. Estimate the amplitude of oscillation for a Cu atom and compare with the inter atomic distance. For the purpose of this calculation you may use the Einstein model. The Einstein temperature for Cu is 240 K.

5.13. The heat capacity of diamond is given below for a few temperatures.

$T(K)$	C_v(J/kmolK)
100	290
150	1060
200	2340

(a) Verify the Debye T^3 law.

(b) Calculate the Debye temperature.

5.14. What is minimum wavelength for waves traveling in [100] and [111] directions in an FCC lattice?

6 The Free Electron Model

6.1. Explain the distinction between localised (or core) and delocalised electrons in solids. Describe two experimental methods of testing the difference between the two types of electrons.

6.2. The conduction electrons in a metal are better described as a plasma than an ordinary gas. In what essential ways does a plasma differ from a gas? Compare the density of electrons in Li and the density of molecules in air.

6.3. Trace the steps which show that the electrical current of the electrons is in the same direction as the field, even though the particles are negatively charged.

6.4. Assuming that the conduction electrons in Cu behaves as a classical gas, calculate the average value of the electron speed, and compare the value obtained with the Fermi velocity.

6.5. In a cyclotron resonance experiment, part of the signal is absorbed by the electrons. What happens to this energy when the system is in a steady-state situation?

6.6. Cu has a mass density of 8.95 g/cm^3 and an electrical resistivity of $1.55{\cdot}10^{-8}$ Ωm at room temperature. Assuming that the effective mass is equal to normal electron mass calculate:

(a) The concentration of the conduction electrons.

(b) The relaxation time.

(c) The Fermi energy.

(d) The Fermi velocity

(e) The mean free path at the Fermi level.

6.7. Sodium (Na) has a volume expansion coefficient of $15{\cdot}10^{-5}$ K^{-1}. Calculate the percentage change in the Fermi level E_F as the temperature is raised from 0° C to 300° C.

6.8. Repeat problem 6.7. for silver, whose volume coefficient of expansion is $18.6 \cdot 10^{-5}$ K^{-1}.

6.9. Calculate the Fermi temperatures T_F for Cu and Na. Also calculate T/T_F in each case for $T = 300$ K. The effective electron masses of Cu and Na are 1.0 and 1.2 times the normal mass.

6.10. Estimate the fraction of electrons excited above the Fermi level at $T = 300$ K for Cu and Na.

6.11. Calculate the ratio of electron- to lattice heat capacities for Cu at $T = 0.3$, 4, 20, 77 and 300 K.

Hint: For the two higher temperatures use the Einstein model for the lattice contribution. The Einstein temperature for Cu is 240 K.

6.12. Plot the Fermi-Dirac function $f(E)$ versus the energy ratio E/E_F at room temperature (300 K). Assume that the Fermi energy is independent of temperature. If E_F = 5 eV, determine the energy values at which $f(E) = 0.5$, 0.7, 0.9 and 0.95.

6.13. Cyclotron resonance has been observed in Cu at a frequency of 24 GHz. Given that the effective electron mass is equal to the normal mass compute the value of the applied magnetic field.

6.14. At which temperature is the electronic contribution to the heat capacity C_v equal to the phonon contribution for Ag?

7 Band Theory

7.1. The empty lattice electron energy is obtained by cutting and displacing various segments of the free electron energy curve. Is this rearrangement justifiable for a truly free electron? How do you differentiate between an empty lattice and free space?

7.2. Band overlap is important in the conductivity of polyvalent metals. Do you expect it to take place in a one-dimensional crystal?

7.3. Convince yourself that the shapes of the first Brillouin zones for the FCC and BCC are those given in the text book.

7.4. Show that the number of allowed k-values in a band of a three-dimensional simple cubic lattice is equal to N, the number of unit cells in the crystal.

7.5. Calculate the number of electron states n in a band of a three-dimensional lattice, which contains N number of unit cells in the crystal.

7.6. Show that the first three bands in the empty lattice model in one dimension span the following energy ranges

$$\begin{cases} 0 \leq E_1 \leq \frac{\pi^2\hbar^2}{2m_e a^2} \\ \frac{\pi^2\hbar^2}{2m_e a^2} \leq E_2 \leq \frac{2\pi^2\hbar^2}{m_e a^2} \\ \frac{2\pi^2\hbar^2}{m_e a^2} \leq E_3 \leq \frac{9\pi^2\hbar^2}{m_e a^2} \end{cases} \tag{B.12}$$

7.7. Show that wave vectors, touching the centers of the hexagonal faces of the first zone of the FCC lattice, give rise to Bragg reflection from the (111) atomic planes. The shape of the zone is given in Kittel. Also show that the other faces give rise to reflection from the (200) planes.

7.8. Show similarly that the faces of the zone for the BCC lattice are associated with reflections from the (110) faces. The shape of the zones are shown in the text book.

7.9. Suppose that the crystal potential in a one-dimensional lattice is composed of a series of rectangular wells which surround the atom. Suppose that the depth of each well is V_0 and its width a/5. Using the nearly free electron model, calculate the values of the first three energy gaps.

7.10. (a) Using the free electron model, and denoting the electron concentration by n, show that the radius of the Fermi sphere is given by $k_F = (3\pi^2 n)^{1/3}$.

(b) As the electron concentration increases, the Fermi sphere expands. Show that this sphere begins to touch the faces of the first zone in an FCC lattice when the electron to atom ratio $n/n_a = 1.36$, where n_a is the atom concentration.

(c) Suppose that some of the atoms in a Cu crystal, which has an FCC structure, are gradually replaced by Zn atoms. Considering that Zn is divalent while Cu is monovalent, calculate the atomic ratio of Zn to Cu in a CuZn alloy (brass)

at which the Fermi sphere touches the zone faces. This particular mixing is interesting because the solid undergoes a structural phase change at this concentration ratio.

8 Semiconductors

8.1. In discussing the tetrahedral bond in the group IV semiconductors (and other substances) the so-called bond model is often used, in which each valence electron is localised along the covalent bond line directions joining the atoms. Explain how this may be reconciled with the delocalised band model, in which the electron is described by a Bloch function extending throughout the crystal.

8.2. Do the bond orbitals of the above bonds correspond to the conduction band or the valence band?

8.3. Describe the bond model associated with the electrons in the conduction band of the group IV semiconductors; *i.e.*, state the spatial region(s) in which these electrons reside.

8.4. What does the breaking of a bond correspond to in the band model?

8.5. Which experimental verification do we have of the fact that the electrons associated with the tetrahedral bond are delocalised?

8.6. Does the fact that a sample exhibits intrinsic behaviour necessarily imply that the sample is pure?

8.7. An experimenter measuring the Hall effect in a semiconductor specimen finds to her surprise that the Hall constant is vanishingly small even at room temperature. She asks you to help her to interpret this result. What is the likely reason? An expression for the Hall coefficient with two carrier types involved can be found in the problem section following Ch. 8 in Kittel.

8.8. (a) Compute the concentration of holes and electrons in an intrinsic sample of Si at room temperature. You may take $m_e = 0.7m$ and $m_h = m$.

(b) Determine the position of the Fermi level under these conditions.

8.9. Gallium arsenide has a dielectric constant $\epsilon_r = 13.13$ and you may take $m_e = 0.07m$ and $m_h = 0.09m$.

(a) Determine the donor and acceptor ionisation energies.

(b) Calculate the Bohr radii for bound electrons and holes.

(c) Calculate the temperature at which freeze-out begins to take place in an n-type sample.

8.10. A silicon sample is doped by arsenic donors of concentration $1.0 \cdot 10^{23}$ m^{-3}. The sample is maintained at room i temperature. You may use the same effective masses as in problem 8.8.

(a) Show that the intrinsic electron concentration is negligible compared to the concentration supplied by the donors.

(b) Assuming that all the impurities are ionised, determine the position of the Fermi level.

(c) Describe the effect on the Fermi level if acceptors are introduced in the above sample at a concentration of $6.0 \cdot 10^{21}$ m^{-3}.

8.11. Given these data for Si: $\mu_e = 0.135$ m^2/V·s, $\mu_h = 0.0475$ m^2/V·s , $E_g = 1.1$ eV and the same effective masses as in problem 8.8, calculate

(a) The relaxation times for the electrons and holes.

(b) The intrinsic conductivity at room temperature.

8.12. A sample of an n-doped semiconductor is in the shape of a slab whose length is 5 cm, width 0.5 cm, and thickness 1 mm. When this slab is placed in a magnetic field of 0.6 Wb/m^2 normal to the slab, a Hall voltage of 8 mV develops at a current of 10 mA. Calculate the carrier density.

8.13. A sample of n-type GaAs whose carrier concentration is $1.0 \cdot 10^{16}$ cm^{-3} has the same dimensions, is in the same field, and carries the same current as in problem 8.12.

(a) Calculate the Hall constant in this sample.

(b) Calculate the Hall voltage developed across the sample.

9 Superconductivity

9.1. The superconductor tin has $T_c = 3.7$ K and $B_c = 30.6$ mT at $T = 0$ K. Calculate the critical current for a tin wire of diameter 1 mm at $T = 2$ K. What diameter of wire would be required to carry a current of 100 A?

9.2. A solenoid is used to investigate the resistivity of superconducting Nb_3Zr. The solenoid is 25 cm long with a diameter of 10 cm. It has 984 turns of a Nb_3Zr wire of diameter 0.47 mm. The decay of the current is governed by

$$I(t) = I_0 \exp\left(-\frac{Rt}{L}\right), \tag{B.13}$$

where R is the resistance and L the inductance. The decay was found to be less than 1 per 10^9 in one hour. Deduce an upper limit for the electrical resistivity of superconducting Nb_3Zr.

9.3. Estimate the strength of the electron-phonon interaction for Al and Pb.

9.4. A measurement of the critical temperature T_c for different Hg-isotopes gave the following result:

M (u)	199.5	200.7	202.0	203.3
T_c (K)	4.185	4.173	4.159	4.146

Determine the relation between T_c and M.

9.5. Nb is a type II superconductor with coherence length $\xi = 3.8 \cdot 10^{-8}$ m. An external magnetic field penetrates a type II superconductor along fluxoids with an approximate diameter of 2ξ containing one quantum of flux. Determine the critical field B_{c2} for Nb and compare with the experimental value $B_{c2} = 0.302$ T. Assume that the critical field is reached when the fluxoids are close-packed.

10 Optical and Dielectric Properties

10.1. Estimate threshold energy and wave length for optical inter band transitions in potassium, using the free electron model.

10.2. Calculate the refractive index of NaCl and CsCl, using the Clausius-Mossotti relation. The electronic polarisabilities are $3.23 \cdot 10^{-35}$ cm^3 for Na^+, $3.05 \cdot 10^{-34}$ cm^3 for Cs^+, and $3.28 \cdot 10^{-34}$ cm^3 for Cl^-.

10.3. Sketch the frequency dependence of the polarisability for a crystal with electronic, ionic, and dipolar effects contributing to it.

10.4. Consider a semiclassical model of the ground state of the hydrogen atom in an electric field normal to the plane of the orbital, as shown in the Figure. Show that $\alpha = 4\pi\epsilon_0 a_H^3$ for this model, where a_H is the radius of the unperturbed orbital. Note that if the applied field is in the x-direction, then the x-component of the field of the nucleus at the displaced position of the electron orbit must be equal to the applied field. (The correct quantum mechanical result is larger than this by a factor $\frac{9}{2}$.)

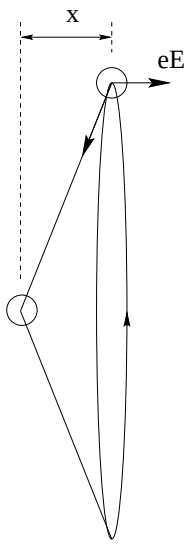

Figure B.2: An electron in a circular orbit of radius a_H is displaced a distance x on application of an electrical field.

10.5. Find the frequency dependence of the electronic polarisability of an electron having the resonance frequency ω_0, treating the system as a simple harmonic oscillator.

11 Magnetic Properties

11.1. The ground state ($1s$) of the hydrogen atom is

$$\psi(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}, \tag{B.14}$$

where a is the Bohr radius. Calculate the diamagnetic molar susceptibility χ_m for this atom, using the Langevin formula.

11.2. Use the Hund rules to determine the ground state and the effective number of Bohr magnetons for:

(a) Eu^{++} with the configuration $4f^7 5s^2 p^6$

(b) Yb^{3+} with the configuration $4f^{13} 5s^2 p^6$

(c) Tb^{3+} with the configuration $4f^8 5s^2 p^6$

11.3. The magnetic susceptibility is measured on a diamagnetic sample, which is suspected to be contaminated by Mn. The measurement gave the following results:

T (K)	300	180	145	115
χ (SI)	$-8.88 \cdot 10^{-6}$	$-8.50 \cdot 10^{-6}$	$-8.24 \cdot 10^{-6}$	$-7.86 \cdot 10^{-6}$

(a) Show that the sample contains a paramagnetic contamination.

(b) Calculate the concentration of Mn under the assumption that they occur as Mn^{2+} ions with ($3d^5$) configuration.

(c) Determine the diamagnetic susceptibility of the substrate.

11.4. Calculate the theoretical saturation magnetisation of $Fe_2(SO_4)_3$, which has a density of $3.1 \cdot 10^3$ kg/m^3.

11.5. In an inhomogeneous magnetic field a body is influenced by a force $F = V\chi H \frac{\partial B}{\partial z}$n the direction of the field gradient. This is used in an experimental setup, where a small amount of the paramagnetic salt ($CrK(SO_4)_2 \cdot 12H_2O$) is attached to a weighting-machine. The turn of the scale was 10.00 mg. Then the salt was sunken into a dewar with liquid nitrogen (77 K) and placed in the inhomogeneous magnetic field with $H\frac{\partial B}{\partial z} = -3.493 \cdot 10^6$ N/m^3. The z axis is vertical. The new turn of the scale was 7.74 mg. The density of the paramagnetic salt is 1.83 g/cm^3 and of liquid nitrogen 0.808 g/cm^3.

(a) Determine the number of effective Bohr magnetons in the paramagnetic salt.

(b) Calculate the theoretical value of effective Bohr magnetons if Cr^{3+} have the configuration $3d^3$.

11.6. Show that the saturation magnetisation just below the Curie temperature is proportional to $(T_c - T)^{-1/2}$, using the mean field approximation and that the spin is 1/2.

C

Solutions, Hints or Answers

1 Crystal Structures

1.1. (a) The primitive basis vectors generates lattice points at the corners and at the faces of a cube so the lattice is an FCC-lattice.

(b) Using the relation $V = |\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|$ we find that $V = a^3/4$.

1.2. Use the vector identity $\mathbf{a} \cdot \mathbf{b} = |\mathbf{a}||\mathbf{b}| \cos\beta$, where β is the angle between the two vectors. Take two cube diagonals given by the vectors $\mathbf{a} = (1, 1, 1)$ and $\mathbf{b} = (1, -1, -1)$. Using the vector identity we find

$$(1, 1, 1) \cdot (1, -1, -1) = \sqrt{3}\sqrt{3} \cos\beta, \tag{C.1}$$

which gives $\beta = 109.47°$. This is the larger angle since the other is $180° - \beta = 70.53°$. Thus the angle between the bonds is $\beta = 109.47°$.

1.3. For the cubic crystals, Al, Fe and Si, the densities are given by the formula

$$\rho = \frac{xM}{N_A}/a^3, \tag{C.2}$$

where x is the number of atoms contained in the cubic unit cell, M the atomic weight, N_A Avogadros number and a the cube length.

Inserting tabled values gives $\rho_{Al} = 2.72 \cdot 10^3$ kg/m^3, $\rho_{Fe} = 7.93 \cdot 10^3$ kg/m^3 and $\rho_{Si} = 2.33 \cdot 10^3$ kg/m^3.

Zn has HCP structure with $a = 2.66$ Å and $c = 4.95$ Å and the primitive cell contains two atoms. The volume of this cell is $ca^2\sqrt{3}/2$ and the density $\rho_{Zn} = 7.17 \cdot 10^3$ kg/m^3.

1.4. Take two tetrahedra, and put them edge on edge with opposite faces parallel and calculate the total height. This gives you c which divided by the length a of a side yields the correct answer.

1.5. The packing ratios are given by:

Structure	Packing ratio
SC	$\pi/6$
BCC	$\sqrt{3}\pi/8$
FCC	$\sqrt{2}\pi/6$
DIAM	$\sqrt{3}\pi/16$

1.6. For a figure see the front page. The primitive cell contains one atom and the cubic cell four atoms.

1.7. Draw a vector $\mathbf{a}$ pointed along say the x-direction and assume it to be a vector of lattice translation. Assume further that a rotation β yielding a vector $\mathbf{a}'$ is a symmetry operation. This means that a rotation of $-\beta$ resulting into the vector $\mathbf{a}''$ also is a symmetry operation. The vector sum $\mathbf{a}' + \mathbf{a}''$ is parallel with $\mathbf{a}$ and is a vector of lattice translation i. e. $\mathbf{a}' + \mathbf{a}'' = n\mathbf{a}$ with n an integer. We have thus that $2a\cos\beta = na$ or that $\cos\beta = n/2$. The only possible values for n are -2, -1, 0, 1 and 2 and none of these produce a lattice that have 5-fold symmetry.

1.8. This is easily seen if you draw a picture. In Fig.C.1 one triangle is reflected in the two mirror planes to generate an object of eight triangles which possesses a 4-fold axis at the intersection.

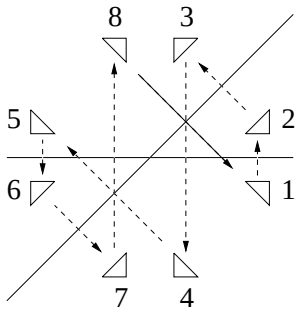

Figure C.1: One triangle reflected in two mirror planes.

1.9. For the (111)-planes every atom has six nearest neighbours and that is the highest possible density. Expressed in the cube length a this density is

$$n = \frac{2\sqrt{12}}{3a^2}. \tag{C.3}$$

For Cu $a = 3.61 \cdot 10^{-10}$ m, giving $n = 0.177 \cdot 10^{20}$ atoms/m^2

1.10. The Miller indices are shown in the table.

Planes	System a	System b
1	(11)	(20)
2	(1$\bar{2}$)	(13)
3	(2$\bar{1}$)	($\bar{1}$3)
4	(31)	(4$\bar{2}$)

2 The Reciprocal Lattice

2.1. Let $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ be the primitive translation vectors of the crystal lattice. Then the reciprocal lattice vectors are given by

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3};\ \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3};\ \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \tag{C.4}$$

Now let $\mathbf{c}_1$, $\mathbf{c}_2$ and $\mathbf{c}_3$ be the reciprocal lattice vectors to the reciprocal lattice. Then we have

$$\begin{aligned}\mathbf{c}_1 &= 2\pi\frac{\mathbf{b}_2\times\mathbf{b}_3}{\mathbf{b}_1\cdot\mathbf{b}_2\times\mathbf{b}_3} = 2\pi\frac{2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}\times 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}}{2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}\cdot 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}\times 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3}} \\ &= V\frac{(\mathbf{a}_3\times\mathbf{a}_1)\times(\mathbf{a}_1\times\mathbf{a}_2)}{(\mathbf{a}_2\times\mathbf{a}_3)\cdot(\mathbf{a}_3\times\mathbf{a}_1)\times(\mathbf{a}_1\times\mathbf{a}_2)}, \qquad \text{(C.5)}\end{aligned}$$

where $V = \mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3$. Recalling the two vector identities

$$\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B}) \qquad \text{(C.6)}$$

$$\mathbf{A}\cdot(\mathbf{B}\times\mathbf{C}) = \mathbf{B}\cdot(\mathbf{C}\times\mathbf{A}) = \mathbf{C}\cdot(\mathbf{A}\times\mathbf{B}), \qquad \text{(C.7)}$$

we find that $\mathbf{c}_1 = \mathbf{a}_1$. In the same way we find that $\mathbf{c}_2 = \mathbf{a}_2$ and $\mathbf{c}_3 = \mathbf{a}_3$ *i.e.* the reciprocal lattice to the reciprocal lattice is the direct lattice.

2.2. Use the relations (C.4) to calculate the reciprocal translation vectors. Note that $\mathbf{a}_i$ must be primitive vectors of the lattice.

(a) The primitive translation vectors of the SC lattice are

$$\mathbf{a}_1 = a\hat{\mathbf{x}}; \quad \mathbf{a}_2 = a\hat{\mathbf{y}}; \quad \mathbf{a}_3 = a\hat{\mathbf{z}}, \qquad \text{(C.8)}$$

which gives

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}; \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}}; \quad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}. \qquad \text{(C.9)}$$

Thus, the reciprocal lattice to the SC lattice is a SC lattice with the lattice constant $2\pi/a$.

(b) The primitive translation vectors of the BCC lattice are

$$\mathbf{a}_1 = \frac{1}{2}a(-\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}}-\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}}+\hat{\mathbf{y}}-\hat{\mathbf{z}}), \qquad \text{(C.10)}$$

which gives

$$\mathbf{b}_1 = \frac{2\pi}{a}(\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{x}}+\hat{\mathbf{z}}); \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}}+\hat{\mathbf{y}}); \qquad \text{(C.11)}$$

Thus, the reciprocal lattice to the BCC lattice is an FCC lattice with the lattice constant $4\pi/a$.

(c) The primitive translation vectors of the FCC lattice are

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{x}}+\hat{\mathbf{z}}); \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}}+\hat{\mathbf{y}}); \qquad \text{(C.12)}$$

which gives

$$\mathbf{b}_1 = \frac{2\pi}{a}(-\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{b}_2 = \frac{2\pi}{a}(\hat{\mathbf{x}}-\hat{\mathbf{y}}+\hat{\mathbf{z}}); \quad \mathbf{b}_3 = \frac{2\pi}{a}(\hat{\mathbf{x}}+\hat{\mathbf{y}}-\hat{\mathbf{z}}), \qquad \text{(C.13)}$$

Thus, the reciprocal lattice to the FCC lattice is a BCC lattice with the lattice constant $4\pi/a$.

2.3. In both cases YES. The angle is 35.26°.

2.4. In the general case the reciprocal lattice vectors depend on all three real lattice vectors. However, for the case when the real lattice vectors are at right angles with one another (simple cubic) the answer is yes.

2.5. Just simple mathematics.

Let $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ be the primitive translation vectors of the crystal lattice. Then the volume is given by $V = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$. The reciprocal lattice vectors are given by equation (C.4) and the volume of the reciprocal cell is

$$\begin{aligned}
\Omega &= |\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3| \\
&= \left| 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \cdot 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \times 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} \right| \\
&= \frac{(2\pi)^3}{V^3} |(\mathbf{a}_2 \times \mathbf{a}_3) \cdot (\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2)| \\
&= \frac{(2\pi)^3}{V^3} |(\mathbf{a}_2 \times \mathbf{a}_3) \cdot \mathbf{a}_1 (\mathbf{a}_3 \cdot \mathbf{a}_1 \times \mathbf{a}_2)| = \frac{(2\pi)^3}{V}. \qquad \text{(C.14)}
\end{aligned}$$

2.6. The volume Ω of the Brillouin zone is equal to the volume of the primitive cell in the reciprocal lattice. The volume is $\Omega = (2\pi)^3/V$, where V is the volume of the primitive cell in the real lattice.

Na has BCC structure with $a = 4.23$ Å. Thus, the volume of the cubic cell is two times V. We find

$$\Omega = \frac{(2\pi)^3}{(4.23 \cdot 10^{-10})^3/2} = 6.55 \cdot 10^{30} \text{ m}^{-3}. \qquad \text{(C.15)}$$

Au has FCC structure with $a = 4.08$ Å. Thus, the volume of the cubic cell is four times V. We find

$$\Omega = \frac{(2\pi)^3}{(4.08 \cdot 10^{-10})^3/4} = 14.6 \cdot 10^{30} \text{ m}^{-3}. \qquad \text{(C.16)}$$

2.7. The first, second and third Brillouin zones of a square lattice are shown in Fig.C.2.

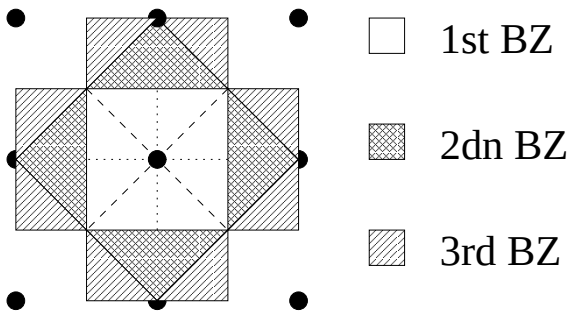

Figure C.2: The first, second and third Brillouin zones of a square lattice.

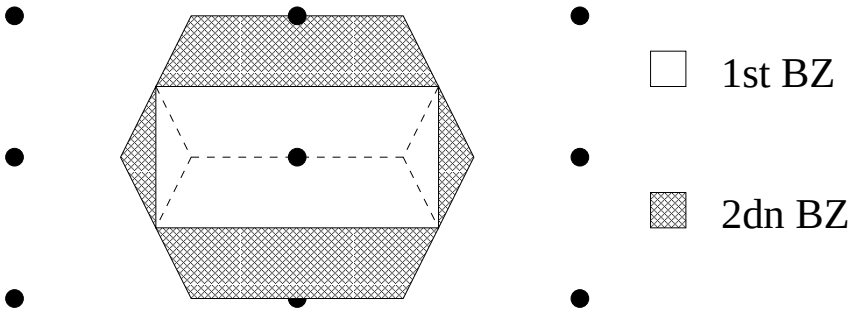

Figure C.3: The first and second Brillouin zones of rectangular lattice.

2.8. The first and second Brillouin zones of the rectangular lattice are shown in Fig.C.3.

2.9. Let $\mathbf{a}_1 = a(1,0)$ and $\mathbf{a}_2 = a(\cos\beta, \sin\beta) = \frac{a}{2}(1,\sqrt{3})$. With the relations

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \Rightarrow \begin{cases} \mathbf{b}_1 \cdot \mathbf{a}_1 &= 2\pi \\ \mathbf{b}_2 \cdot \mathbf{a}_1 &= 0 \\ \mathbf{b}_2 \cdot \mathbf{a}_2 &= 2\pi \\ \mathbf{b}_1 \cdot \mathbf{a}_2 &= 0 \end{cases}, \tag{C.17}$$

we find that the reciprocal lattice vectors are

$$\begin{cases} \mathbf{b}_1 &= \frac{2\pi}{a}(1, -1/\sqrt{3}) \\ \mathbf{b}_2 &= \frac{2\pi}{a}(0, 2/\sqrt{3}) \end{cases}. \tag{C.18}$$

Thus the lattice constant, $b = |\mathbf{b}_1| = |\mathbf{b}_2|$, of the reciprocal lattice is $b = 4\pi/\sqrt{3}a$.

If we use the relation $\mathbf{x} \cdot \mathbf{y} = |x||y|\cos\alpha$ with $\mathbf{x} = \mathbf{b}_1$ and $\mathbf{y} = \mathbf{b}_2$ we find that the angle between $\mathbf{b}_1$ and $\mathbf{b}_2$ is 120° *i.e.* the reciprocal lattice is hexagonal. With the same relation using $\mathbf{x} = \mathbf{a}_1$ and $\mathbf{y} = \mathbf{b}_1$ we find that the reciprocal lattice is rotated by 30° relative to the real lattice.

2.10. With $\mathbf{a}_1 = a(1,0)$ and $\mathbf{a}_2 = a(-1,\sqrt{3})$ and the relations (C.17), we find that the reciprocal lattice vectors are

$$\begin{cases} \mathbf{b}_1 &= \frac{2\pi}{a}(1, 1/\sqrt{3}) \\ \mathbf{b}_2 &= \frac{2\pi}{a}(0, 1/\sqrt{3}) \end{cases}. \tag{C.19}$$

2.11. The shortest distance D from the origin to the first BZ boundary is given by

$$D = \frac{|\mathbf{G}_{min}|}{2}, \tag{C.20}$$

where $\mathbf{G}_{min}$ is the shortest reciprocal lattice vectors.

Li has BCC structure with $a = 3.49$ Å. The primitive translation vectors of the reciprocal lattice are given by (C.11) in problem 2.2. Thus

$$|\mathbf{G}_{min}| = \frac{2\pi}{a}\sqrt{2} \Rightarrow \tag{C.21}$$

$$D = \frac{2\pi\sqrt{2}}{2 \cdot 3.49 \cdot 10^{-10}} = 1.27 \cdot 10^{10}\mathrm{m}^{-1}. \tag{C.22}$$

Ag has FCC structure with $a = 4.09$ Å. The primitive translation vectors of the reciprocal lattice are given by (C.13) in problem 2.2. Thus

$$|\mathbf{G}_{min}| = \frac{2\pi}{a}\sqrt{3} \Rightarrow \tag{C.23}$$

$$D = \frac{2\pi\sqrt{3}}{2 \cdot 4.09 \cdot 10^{-10}} = 1.33 \cdot 10^{10}\mathrm{m}^{-1}. \tag{C.24}$$

3 Diffraction in Crystals

3.1. The size of the sample is much smaller than the distance from the sample to the detector.

3.2. Let a photon collide with a free electron initially at rest. After the collision the photon moves in the opposite direction but has lost some of its energy to the electron. The law of conservation of momentum is given by

$$\frac{h}{\lambda} = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}} - \frac{h}{\lambda'} \tag{C.25}$$

and the law of conservation of energy by

$$\frac{hc}{\lambda} + m_0 c^2 = \frac{hc}{\lambda'} + \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}}. \tag{C.26}$$

Put the terms containing the velocity v on one side of the equal sign and eliminate v after having squared both equations. After some algebra !!! you will find that the change in wavelength of the photon is given by

$$\lambda' - \lambda = \frac{2h}{m_0 c} \approx 0.0485 \text{ Å}. \tag{C.27}$$

For a typical X-ray wavelength of 1 Å we can observe a change of about 5 % but this is for a free electron in vacuum. In a crystal most electrons are tied to the nucleus and then the change in wave length is much smaller. The assumption of elastic scattering is thus a good approximation.

3.3. Take a plane-wave field given by $u = A\exp\{i(k \cdot r - \omega t)\}$ incidenting on an electron. The scattered field is an outgoing spherical wave represented by $u' = f_e \cdot \frac{A}{D}\exp\{i(kD - \omega t)\}$. Here D is the distance from the electron to the detector and f_e a parameter known as the scattering length of the electron. The intensity of the outgoing field is given by $|u'|^2$, which we see is proportional to $1/D^2$. Multiplying with the area $4\pi D^2$ shows that the energy is independent of D which it must be as there is no accumulation of energy in free space.

3.4. Much simpler mathematics.

3.5. Yes, but the atomic form factors differ as the number of atomic electrons differs.

3.6. The reason is that the mass of a neutron is much larger than the mass of an electron. Convince yourself of that by comparing the energies for one and the same de Broglie wave length.

3.7. Of course not. Since $\lambda_{light} \approx 10^{-6} - 10^{-7}$ m and the distance between atoms in a crystal is $\approx 10^{-10}$ m.

3.8. The neutron is uncharged an can penetrate much deeper into the crystal.

3.9. The minimum wavelength is obtained when the electron gives all of its kinetic energy to the photon. Thus the energy E of these photons is equal to the kinetic energy of the electrons

$$E = \frac{hc}{\lambda} = 10 \text{ keV}. \tag{C.28}$$

3.10. First show that for a simple cubic lattice there is no extinction rule. Then, using Bragg's law

$$\frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta = \lambda, \tag{C.29}$$

we find

Plane:	(100)	(110)	(111)	(200)	(210)	(211)
Bragg angle:	17.1°	24.6°	30.6°	36.0°	41.1°	46.0°

3.11. (a) $d(111) = 2.34$ Å

(b) First calculate the cube length a with the formula

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{C.30}$$

and recall that the cubic cell contains four atoms. We simply have that

$$\rho = \frac{4 \cdot 27}{N_A a^3}, \tag{C.31}$$

from which we find that $N_A = 6.0 \cdot 10^{26}$ kmol^{-1}.

3.12. (a) From Bragg's law (C.30), we easily obtain that $a = 2.91$ Å.

(b) Reflections from the (111)-planes are forbidden since $1 + 1 + 1 = 3$ is an odd number.

(c) The density is given by

$$\rho = \frac{2M/N_A}{a^3} = 7544 \text{ kg/m}^3 \tag{C.32}$$

3.13. For a spherically symmetric electron distribution the atomic form factor is given by

$$f = 4\pi \int dr \rho(r) r^2 \frac{\sin Gr}{Gr}. \tag{C.33}$$

Use Euler's formula

$$\sin Gr = \frac{e^{iGr} - e^{-iGr}}{2i} \tag{C.34}$$

and integrate by parts.

3.14. We know that central diffraction maxima occur for $\mathbf{a}\cdot\Delta\mathbf{k} = h\cdot 2\pi$, where h is an integer. The first minimum occurs for $\frac{1}{2}M(\mathbf{a}\cdot\Delta\mathbf{k}) = \pi$ and the second for $\frac{1}{2}M(\mathbf{a}\cdot\Delta\mathbf{k}) = 2\pi$, the first subsidiary maximum is then likely to be found for $\frac{1}{2}M(\mathbf{a}\cdot\Delta\mathbf{k}) = \frac{3\pi}{2}$. This gives an intensity of $0.045M^2$, in the limit of large M.

3.15. Use the relation

$$S_{hkl} = \sum_i f_i e^{-2\pi i(hx_i+ky_i+lz_i)} \tag{C.35}$$

where the sum is over all atoms i in the unit cell.

With one atom in (0,0,0) and one in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ we obtain

$$S_{hkl} = f_a\left(1+e^{-i\pi(h+k+l)}\right). \tag{C.36}$$

With one eight of an atom at the positions (0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0), (1,0,1), (0,1,1) , (1,1,1) and one atom at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ we obtain

$$S_{hkl} = \frac{f_a}{8}\left(1+e^{-i2\pi h}+e^{-i2\pi k}+e^{-i2\pi l}+e^{-i2\pi(h+k)}+e^{-i2\pi(h+l)}+ \right. \\ \left. +e^{-i2\pi(k+l)}+e^{-i2\pi(h+k+l)}\right)+f_a e^{-i\pi(h+k+l)}. \tag{C.37}$$

Which after simplification is the same formula as which results when assuming the cell to contain one atom at a corner and another at the center.

3.16. Using the relation (C.35) for BCC we find the extinction rule $h+k+l =$ even, *i.e.* we have reflections from the (110)-, (200)- and (220)-planes.

Using the relation (C.35) for FCC we find the extinction rule all h,k,l even or all h,k,l odd, *i.e.* we have reflections from the (111)-, (200)- and (220)-planes.

3.17. Diamond structure is an FCC lattice plus a basis in (0,0,0) and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. From the relation (C.35) we get that

$$\begin{aligned} S^{Dia}_{hkl} &= f_a\sum_j\left(e^{-i2\pi(hx_j+ky_j+lz_j)}+e^{-i2\pi\{h(x_j+\frac{1}{4})+k(y_j+\frac{1}{4})+l(z_j+\frac{1}{4})\}}\right) \\ &= S^{FCC}_{hkl}\left(1+e^{-\frac{i\pi}{2}(h+k+l)}\right), \end{aligned} \tag{C.38}$$

where the j is the four lattice points of the cubic FCC cell. From this we see that $S^{Dia}_{hkl}\neq 0$ provided that all h, k, l even and $h+k+l = 4n$ or all h, k, l odd. Thus the (111)- and (220)-planes in problem 3.16 are allowed.

3.18. Put one atom in $(0,0,0)$ (Cs) and the other in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ (Cl), then the structure factor (C.35) is

$$S_{hkl} = f_{Cs}+f_{Cl}e^{-i\pi(h+k+l)} \approx f_{Cl}\left(3+e^{-i\pi(h+k+l)}\right)\neq 0 \ \ \forall \ \ hkl. \tag{C.39}$$

In spite of the fact that the structure is similar to BCC it is a SC-structure with a basis of two atoms. Therefore the extinction rule for the BCC lattice is violated.

3.19. Differentiate the Bragg law $2L\sin\theta = \lambda$ and you will obtain $L\cos\theta\cdot d\theta + dL\sin\theta = 0$ or $d\theta = -\frac{dL}{L}\tan\theta$. Also differentiate $V = L^3$ and you will find the desired result.

3.20. All h, k, l odd or all even for allowed reflections, since Ni has FCC structure. The three smallest angles result from reflections from the (111)-, (200)- and (220)-planes. 150 eV electrons allows a classical evaluation of the de Broglie wave length, so $\lambda = h/\sqrt{2Em} = 1.00$ Å. Using the lattice parameter $a = 3.52$ Å one finds:

Plane	(111)	(200)	(220)
Angle	14.2°	16.5°	23.7°

3.21. The structure and extinction rules are:

Substance	Structure	Extinction rule
NaCl	FCC	$\forall \quad h,k,l$ even $\forall \quad h,k,l$ odd
CsCl	SC	$\forall \quad h,k,l$
Diamond	Diamond	$\forall \quad h,k,l$ even, $h+k+l=4n$ $\forall \quad h,k,l$ odd

If we take the square of Bragg's law we find

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2+k^2+l^2), \tag{C.40}$$

where $\lambda^2/4a^2$ is a constant and $(h^2+k^2+l^2)$ is an integer. Putt $(h^2+k^2+l^2) = X$ and calculate the fractions

$$\frac{\sin^2\theta_i}{\sin^2\theta_1} = \frac{X_i}{X_1}. \tag{C.41}$$

Now we can identify (hkl) for the scattering planes.

Sample A				Sample B				Sample C			
θ	$\frac{\sin^2\theta_i}{\sin^2\theta_1}$	X_i	(hkl)	θ	$\frac{\sin^2\theta_i}{\sin^2\theta_1}$	X_i	(hkl)	θ	$\frac{\sin^2\theta_i}{\sin^2\theta_1}$	X_i	(hkl)
10.8°	1	1	100	13.7°	1	3	111	22.0°	1	3	111
15.3°	2	2	110	15.9°	4/3	4	200	37.7°	8/3	8	220
18.9°	3	3	111	22.8°	8/3	8	220	45.8°	11/3	11	311
22.0°	4	4	200	27.0°	11/3	11	311	59.8°	16/3	16	400
24.7°	5	5	210	28.3°	12/3	12	222	70.4°	19/3	19	331

When we compare the scattering planes with the extinction rules we find that sample A is CsCl, sample B is NaCl and that sample C is diamond.

4 Crystal Binding

4.1. For a silicon atom the electron configuration is (Ne)$3s^2 3p^2$. Thus Si has four valence electrons and lacks four electrons with respect to a filled shell structure (Ar). Such a structure can however be simulated by electron sharing. First promote one of the

s-electrons to have p-character. This promotion to (Ne)$3s^1 3p^3$ costs energy but this cost is more than regained when the bonds are formed. Construct the hybrids

$$\begin{cases} \phi_1 &= s + p_x + p_y + p_z \\ \phi_2 &= s + p_x - p_y - p_z \\ \phi_3 &= s - p_x - p_y + p_z \\ \phi_4 &= s - p_x + p_y - p_z \end{cases}, \tag{C.42}$$

from the atomic orbitals above and you will find that the angle between them are 109.47° which is the angle between the bonds in the diamond structure. The directed orbitals form four covalent bonds each containing two electrons shared by the the involved atoms. This means that each atom has an Ar-like electron environment and this leads to strong bonds. A full understanding of this type of bond, however, require rather elaborate quantum mechanics.

4.2. With $r = 2260$ kJ/kg (heat of vaporisation for water), $N_A = 6.02 \cdot 10^{26}$ kmol^{-1} (Avogadros number) and $M = 18$ kg/kmol we obtain

$$E_b = \frac{Mr}{N_A} = 0.42 \text{ eV/molecule}. \tag{C.43}$$

4.3. Consider the dipole in Fig.C.4 for which d and L distances and q is the charge. The net force between the dipoles is readily obtained to be

$$F = \frac{q^2}{4\pi\epsilon_0}\left(-\frac{1}{L^2} - \frac{1}{(L+2d)^2} + \frac{2}{(L+d)^2}\right), \tag{C.44}$$

simplify this expression and show that F is negative.

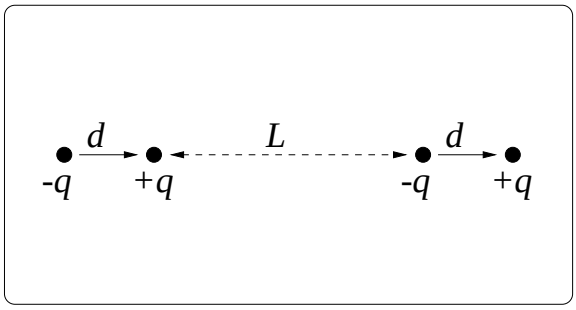

Figure C.4: Two parallel dipoles.

4.4. The potential for a linear harmonic oscillator is $V(x) = Cx^2/2$, so the Hamiltonian of two non-interacting oscillators is

$$H_0 = \frac{1}{2m}p_1^2 + \frac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Cx_2^2. \tag{C.45}$$

The frequency ω_0 of one of the oscillators is $\omega_0 = \sqrt{C/m}$ and the zero point energy of the system is $E_0 = \hbar\omega_0$. Let H_1 be the coulomb interaction energy of the two oscillators. This is given by

$$H_1 = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} + \frac{1}{R+x_1-x_2} - \frac{1}{R+x_1} - \frac{1}{R-x_2}\right) \approx -\frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}, \tag{C.46}$$

when $|x_1|, |x_2| \ll R$. From this one get

$$H = H_0 + H_1 \approx \frac{1}{2m}p_1^2 + \frac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Cx_2^2 - \frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}. \tag{C.47}$$

The Hamiltonian H may be written in the form of two non-interacting oscillators if one uses the coordinate transformation

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2); \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2). \tag{C.48}$$

Thus

$$H \approx \left(\frac{1}{2m}p_s^2 + \frac{1}{2}C_s x_s^2\right) + \left(\frac{1}{2m}p_a^2 + \frac{1}{2}C_a x_a^2\right). \tag{C.49}$$

where

$$C_s = C - \frac{2e^2}{4\pi\epsilon_0 R^3} \text{ and } \quad C_a = C + \frac{2e^2}{4\pi\epsilon_0 R^3}. \tag{C.50}$$

The frequencies are therefore given by

$$\omega_{a,s} = \sqrt{\frac{C \pm \frac{2e^2}{4\pi\epsilon_0 R^3}}{m}} = \omega_0\sqrt{1 \pm \frac{2e^2}{4\pi\epsilon_0 R^3 C}} \approx \omega_0\left(1 \pm \frac{1}{2}\frac{2e^2}{4\pi\epsilon_0 R^3 C}\right), \tag{C.51}$$

using the first two terms in the Taylor series of $\sqrt{1+x}$. The zero point energy of this system is $\frac{1}{2}\hbar(\omega_s + \omega_a)$, so the binding energy is

$$E_b = E_0 - \frac{1}{2}\hbar(\omega_s + \omega_a) \approx \frac{\hbar\omega_0}{8}\left(\frac{2e^2}{4\pi\epsilon_0 R^3 C}\right)^2 \sim \frac{1}{R^6}. \tag{C.52}$$

4.5. Use equation (C.43). For Ne, $r = 86$ kJ/kg and $M = 20.183$ kg/kmol which yields a binding energy of 0.018 eV/atom.

4.6. (a) At equilibrium

$$\left(\frac{dE}{dR}\right)_{R=R_0} = 0. \tag{C.53}$$

We find that

$$\frac{dE}{dR} = -N\frac{An}{R^{n-1}} + N\frac{\alpha e^2}{4\pi\epsilon_0 R^2} \tag{C.54}$$

and when we insert $R = R_0$ from equation (B.7), we find $\left(\frac{dE}{dR}\right)_{R=R_0} = 0$.

(b) Form the relation (B.6), we find that

$$E(R_0) = N\frac{A\alpha e^2}{4\pi\epsilon_0 AnR_0} - N\frac{\alpha e^2}{4\pi\epsilon_0 R_0} = -\frac{\alpha e^2 N}{4\pi\epsilon_0 R_0}\left(1 - \frac{1}{n}\right). \tag{C.55}$$

(c) From equation (C.55) we find

$$\frac{1}{n} = \left(1 + \frac{E4\pi\epsilon_0 R_0}{\alpha e^2 N}\right). \tag{C.56}$$

With $R_0 = a/2$, where $a = 5.63$ Å, we get $n = 0.530$.

5 Lattice Vibrations

5.1. The solutions are of the form $u(x) = Ae^{ikx}$. The boundary condition $u(0) = u(L)$ gives $k = n \cdot 2\pi/L$, $n = 1, 2, 3$ and the boundary condition $u(0) = u(L) = 0$ gives $k = n \cdot \pi/L$, $n = 1, 2, 3$. Figure C.5 shows $\mathrm{Im}(u) = \mathrm{Im}(Ae^{ikx})$ in the interval $x = [0, L]$.

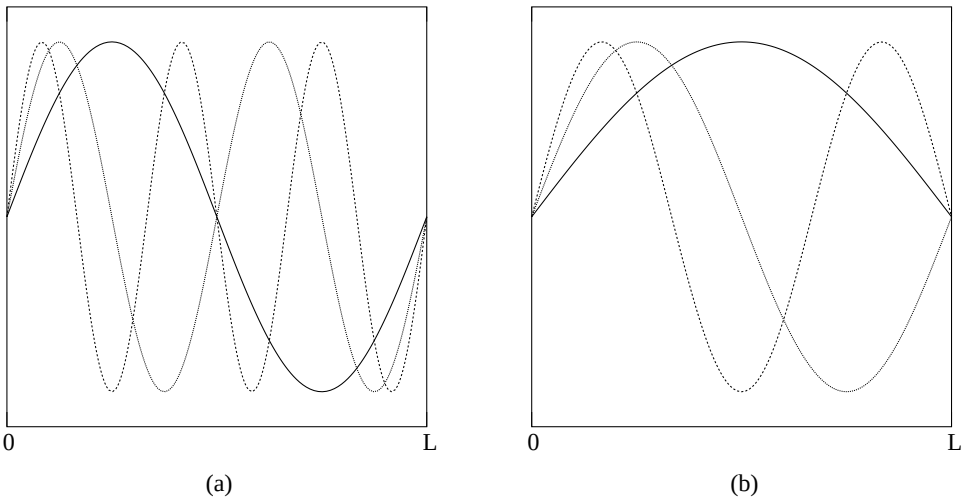

Figure C.5: The three first modes under the boundary conditions $u(0) = u(L)$ (a) and $u(0) = u(L) = 0$ (b).

5.2. Apply periodic boundary conditions over a square of side L. This leads to a k-vector density of $(L/2\pi)^2$ and that $2\pi k dk \cdot (L/2\pi)^2 = D(\omega)d\omega$. After simplification $D(\omega) = A\omega/(2\pi v^2)$, where A is the area and v the velocity of sound.

5.3. According to the Einstein model the atom energy in one dimension is given by

$$E_{Atom} = \frac{\sum_{n=0}^{\infty} n\hbar\omega e^{-n\hbar\omega/k_BT}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega}} = \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}, \tag{C.57}$$

resulting in the crystal energy $U = 3N_A E_{Atom}$. We see that we multiply the thermal energy for one atom with the total number of atoms *i.e.* we assume that the atoms vibrate independent of one another.

In the Debye model the crystal energy is given by

$$U = \int_0^{\omega_D} n(\omega) \cdot \hbar\omega \cdot D(\omega)d\omega \tag{C.58}$$

where

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_BT} - 1} \text{ (Bose-Einstein statistics)} \tag{C.59}$$

We sum (or integrate) over a continuum of modes with energies $\hbar\omega$ but assume that the modes do not interact with one another.

5.4. No, the wave length of sound is much larger than a molecule. The sound velocity in a gas is the velocity of a pressure pulse.

5.5. The interatomic attractive force results from an reorganisation of the outer electrons of the atoms. This means that they have to be close to one another for the electron clouds to overlap. This also explains why the free atom model holds so well in gases in which the average interatomic distance is much large than the corresponding distance in a crystal.

5.6. The dispersion relation is given by

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{Ka}{2} \right|, \tag{C.60}$$

see Kittel for details. In Fig. C.6 ω is in units of $\sqrt{4C/M}$.

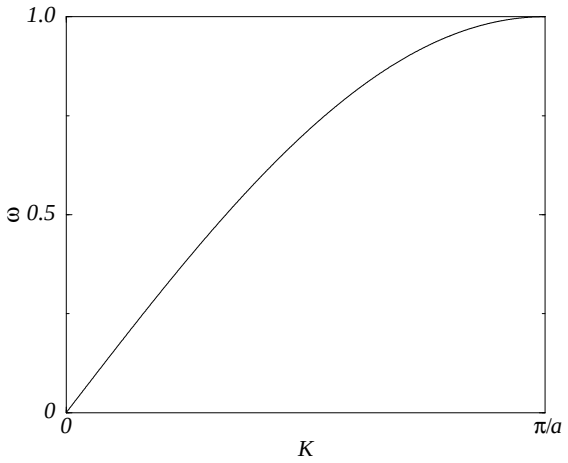

Figure C.6: The dispersion relation of a one-dimensional crystal with one atom per cell.

5.7. The roots are given by

$$\omega^2 = C\frac{M_1 + M_2}{M_1 M_2} \pm C\sqrt{\left(\frac{M_1 + M_2}{M_1 M_2}\right)^2 - \frac{4\sin^2 \frac{Ka}{2}}{M_1 M_2}} \tag{C.61}$$

At the zone center we have $K = 0$, so we find

$$\begin{aligned} \omega^2 &= 2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \quad \text{(optical branch)} \\ \omega^2 &= 0 \qquad\qquad\qquad\quad \text{(acoustical branch).} \end{aligned} \tag{C.62}$$

At the zone boundary $K = \pm\pi/a$, we find

$$\omega^2 = \frac{2C}{M_1}; \qquad \omega^2 = \frac{2C}{M_2}. \tag{C.63}$$

The dispersion relation is shown in Fig. C.7.

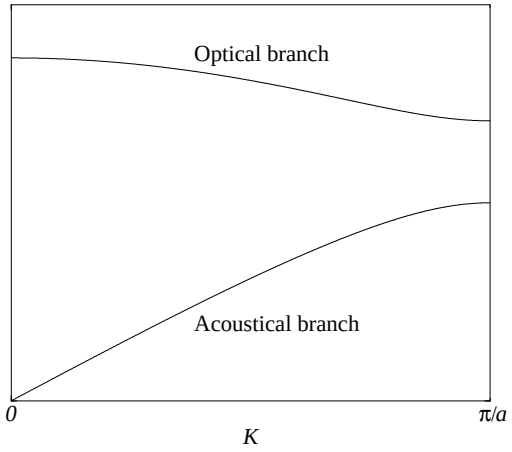

Figure C.7: The dispersion relation of a one-dimensional crystal with two atom per cell.

5.8. Applying periodic boundary conditions over a chain of total length L containing N cells with a primitive translation vector $\mathbf{a}$ gives a k-vector density of $L/2\pi = Na/2\pi$. Multiplying this with the length of the Brillouin zone ($= 2\pi/a$) results in $(Na/2\pi)\cdot(2\pi/a) = N$ allowed modes. For a diatomic lattice we have two branches, the acoustical and the optical branch. Therefore there are $2N$ allowed modes.

5.9. The frequency gap disappears, since the gap is given by $|\sqrt{2C/M_2} - \sqrt{2C/M_1}|$.

5.10. The density of states in one dimension is given by

$$D(\omega) = \frac{L}{\pi}\left(\frac{d\omega}{dk}\right)^{-1} = \frac{L}{\pi\nu}, \tag{C.64}$$

in the Debye approximation. The number of allowed modes in the acoustic branch is

$$\int_0^{\omega_D} D(\omega)d\omega = N, \tag{C.65}$$

which gives

$$\omega_D = \frac{N\pi\nu}{L} \Rightarrow D(\omega) = \frac{N}{\omega_D}. \tag{C.66}$$

Now we can use the relation

$$C_v^{acoustic} = \frac{dU}{dT}. \tag{C.67}$$

After differentiation, the change to the dimensionless variable $x = \hbar\omega/k_BT$ and by defining the Debye temperature θ_D as $k_B\theta_D = \hbar\omega_D$ the expression for the heat capacity takes the form

$$C_v^{acoustic} = R\frac{T}{\theta_D}\int_0^{\theta_D/T} \frac{x^2e^x}{\left(e^x-1\right)^2}dx. \tag{C.68}$$

At low temperatures, $T \ll \theta_D$, the upper limit of the integral approaches ∞, and in this limit

$$C_v^{acoustic} = R\frac{T}{\theta_D}\cdot\frac{\pi^2}{3}. \tag{C.69}$$

This shows a linear behaviour. Please note that at low temperatures no optical phonons are excited. At high temperatures these have to be included. Here it can be assumed that the Einstein model works well, since ω is independent of k in this model. Thus in the high temperature limit we obtain

$$\begin{aligned} C_v^{tot} &= C_v^{acoustic} + C_v^{opt} \\ &= R\frac{T}{\theta_D}\int_0^{\theta_D/T} \frac{x^2 e^x}{(e^x-1)^2}dx + R\left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T}-1)^2}. \end{aligned} \quad \text{(C.70)}$$

For $T \gg \theta_D$ and $k_B T \gg \hbar\omega_E$ we simply obtain $C_v^{tot} \to 2R$ (show that).

5.11. (a) For the crystal we have $U = 3N_A k_B T = 3RT$ and thus that $C_v = 3R$, i. e. constant for all elements, but this is the molar heat capacity. The specific heat capacity is obtained after dividing with the atomic weight thus $C_v^{spec} = 3R/M$. For Cu we find $C_v^{spec} = 392$ J/kgK, which is close to the experimental value $C_v^{spec} = 385$ J/kgK. For diamond we find $C_v^{spec} = 2.08$ kJ/kgK, which is fare from the experimental value $C_v^{spec} = 509$ J/kgK. Comparing with experimental values at room temperature one finds good agreement for Cu but a complete failure for diamond. This is due to the fact that $\theta_D = 343$ K for Cu and $\theta_D = 2230$ K for diamond. Since the Debye temperature of diamond is much higher than the room temperature the classical theory fails.

(b) The atom energy is

$$E_{Atom} = 3k_B\theta_D \approx 0.09 \text{ eV}. \quad \text{(C.71)}$$

(c) From the relation

$$C_v = \left(\frac{dU}{dT}\right)_v \Rightarrow dU = C_v(T)dT, \quad \text{(C.72)}$$

we find

$$\begin{aligned} U &= \int_0^{\theta_D} C_v(T)dT = \frac{1}{2}\{C_v(\theta_D) - C_v(0)\}\theta_D \\ &\approx \frac{1}{2}(3R-0)\theta_D = \frac{3R\theta_D}{2} \\ &\Rightarrow E_{Atom} = \frac{3}{2}k_B\theta_D \approx 0.044 \text{ eV}. \end{aligned} \quad \text{(C.73)}$$

But this is just half of the classical value, why? We have to include the zero point energy. Approximating the zero point frequency with the Debye frequency this energy is given by

$$\frac{3}{2}\hbar\omega_D = \frac{3}{2}k_B\theta_D. \quad \text{(C.74)}$$

Adding this to the integrated value above one obtains agreement with the classical value. It might be argued, however, that taking the zero point frequency to be equal to the Debye frequency is an overestimation. Instead it might be more realistic to calculate an average frequency using the Debye model. This is easily performed remembering that the density of states $D(\omega) \sim \omega^2$, thus

$$\omega_{av} = \frac{\int_0^{\omega_D} \omega D(\omega)d\omega}{\int_0^{\omega_D} D(\omega)d\omega} = \frac{3\omega_D}{4}. \quad \text{(C.75)}$$

We then obtain

$$E_{atom}^{zero} = \frac{3}{2}\hbar \cdot \frac{3\omega_D}{4} = \frac{9}{8}\hbar\omega_D = \frac{9}{8}k_B\theta_D. \tag{C.76}$$

Now we have $E_{Atom} = \frac{21}{8}k_B\theta_D$ as a total estimate which is 87.5 % of the classical value.

5.12. For an ideal gas, $C_v = \frac{3R}{2}$, while for Cu $C_v = 3R$. For an ideal gas the molecules have only kinetic energy while in a solid the Einstein model assumes that the atoms are coupled to each other with springs. The atoms thus have both kinetic and potential energy. On the average these energies are equal. Thus

$$E_{atom}^{pot} = \frac{3}{2}k_B\theta_D. \tag{C.77}$$

But the energy of a spring is given by $\frac{1}{2}Cx^2$. Here C is the spring constant and x the average displacement from equilibrium. But

$$\omega_E = \sqrt{\frac{C}{m}} \Rightarrow C = m\omega_E^2 \text{ (recall classical physics).} \tag{C.78}$$

Thus

$$\frac{3}{2}k_B\theta_E = \frac{1}{2}m\omega_E^2x^2 \Rightarrow x^2 = \frac{3k_B\theta_E}{m\omega_E^2}. \tag{C.79}$$

Using the identity, $\hbar\omega_E = k_B\theta_E$, and that $m = M/N_A$ one finally obtains

$$x = \sqrt{\frac{3\hbar^2N_A}{Mk_B\theta_E}} \approx 0.1 \text{ Å}. \tag{C.80}$$

5.13. (a) According to the Debye T^3-law the heat capacity is given by

$$C_v \approx \frac{12\pi^4}{5}R\left(\frac{T}{\theta_D}\right)^3. \tag{C.81}$$

Plot C_v against T^3 and show the linear behaviour.

(b) Estimate the slope of the curve and from that, the Debye temperature can found to be around 1900 K. This is lower than the value quoted in the text book of 2230 K, but we have to remember that this value is given to yield the best possible fit to experimental data for the entire temperature range.

5.14. The Brillouin zone (BZ) of the FCC lattice can be found in the text book. In the [100]-direction the distance from the center of the BZ to the boundary is $\frac{2\pi}{a}$ while the corresponding distance along the [111]-direction is half of a reciprocal lattice vector or $\frac{1}{2}\frac{2\pi}{a}\sqrt{3} = \frac{\pi}{a}\sqrt{3}$. Remembering that $\lambda = \frac{2\pi}{k}$ we easily find that $\lambda_{[100]} = a$ and $\lambda_{[111]} = \frac{2a}{\sqrt{3}}$. Why are these wave lengths the smallest possible?

6 The Free Electron Model

6.1. A core, or inner shell electron has a probability distribution which is large near the nucleus but weak or nearly zero midway between the atoms. A free or delocalised electron on the other hand has a wave function very much like a plane wave. Such electrons contribute to electrical- and thermal conductivity while core electrons do not. The existence of core electrons is, however, clear from X- ray diffraction experiments. Remember the atomic form factor.

6.2. Electrons are charged particles while a gas usually consists of uncharged molecules or atoms. From the ideal gas equation $pV = NRT$ we find that $n = N/V \approx 2.4 \cdot 10^{25}$ molecules/m^3. For Li which has BCC structure and one valence electron per atom we find that the electron density is $n \approx 4.7 \cdot 10^{28}$ electrons/m^3. Thus the electron density is much greater than the density of molecules in air.

6.3. The electric current density is given by $\mathbf{J} = Nq\mathbf{v}$. In an electrical field we realise that changing the sign of the charge is accompanied by a reversed direction of the velocity i. e. the sign of $\mathbf{J}$ is the same.

6.4. Classically we have $E_{electron} = 3k_BT/2$. For $T = 300$ K we easily find the velocity to be $v = 1.2 \cdot 10^5$ m/s. Compare this with $v_F = 1.57 \cdot 10^6$ m/s.

6.5. For an external electric AC - field, with a frequency coinciding with the cyclotron frequency, strong absorption of the signal can be observed and the sample absorbs energy and the velocity of the excited electrons increases. In the steady state this velocity reaches a constant value limited by collisions with phonons and impurities and a balance between absorbed energy and energy leaving the sample through radiation exists.

6.6. (a) The electron density, n, is given by

$$n = Z_v \frac{N_A}{V}, \tag{C.82}$$

where Z_v is the valence of the metal and V is the volume of 1 kmol. But $V = M/\rho$, thus we obtain

$$n = Z_v \frac{\rho N_A}{M} = 8.48 \cdot 10^{28} \text{ m}^{-3}. \tag{C.83}$$

(b) $\tau = 2.7 \cdot 10^{-14}$ s

(c) $E_F = 7.0$ eV

(d) $v_F = 1.57 \cdot 10^6$ m/s

(e) $l_F = v_F\tau \approx 400$ Å

6.7. $E_F = \frac{\hbar^2}{2m}(3\pi^2 N/V)^{2/3}$ and when $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ we realise that the Fermi energy decreases when the temperature increases. Differentiate the expression for E_F and you will find that

$$\frac{dE_F}{E_F} = -\frac{2}{3}\frac{dV}{V} = -\frac{2}{3}\beta\Delta T. \tag{C.84}$$

Here we have assumed that β is constant. Calculation shows a decrease of 3 %.

6.8. Identical calculations as above shows a decrease of 3.7 % .

6.9. See definition of the Fermi temperature T_F in the text book. We conclude that room temperature is much lower than T_F.

6.10. The fraction of electrons excited above the Fermi level is given by the integral

$$\eta = \frac{1}{N}\int_{E_F}^{\infty} D(E)f(E,T)dE, \tag{C.85}$$

where

$$f(E,T) = \frac{1}{e^{(E-E_F)/k_BT}+1}, \tag{C.86}$$

i. e. we replace the chemical potential μ with the constant E_F (see argument in the text book). Further we have

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \tag{C.87}$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}. \tag{C.88}$$

From the expressions for $D(E)$ and E_F we eliminate $\frac{\hbar^2}{2m}$ to obtain

$$D(E) = \frac{3N}{2E_F^{3/2}}E^{1/2} \tag{C.89}$$

and as the main contribution to the integral results for energies very near E_F we can make the approximation

$$D(E) = D(E_F) \approx \frac{3N}{2E_F}. \tag{C.90}$$

It follows then that

$$\eta \approx \frac{3}{2E_F}\int_{E_F}^{\infty} \frac{dE}{e^{(E-E_F)/k_BT}-1}. \tag{C.91}$$

Introducing the dimensionless variable $x = (E - E_F)/k_BT$ we obtain the simpler expression

$$\eta = \frac{3k_BT}{2E_F}\int_0^{\infty} \frac{dx}{e^x+1}, \tag{C.92}$$

which can be solved analytically. Putting $y = e^x$ we get

$$\int_0^{\infty}\frac{dx}{e^x+1} = \int_1^{\infty}\frac{dy}{y(y+1)} = \int_1^{\infty}\left(\frac{1}{y}-\frac{1}{y+1}\right)dy = \ln 2. \tag{C.93}$$

Thus

$$\eta = \frac{3\ln 2}{2}\frac{k_BT}{E_F} \approx \frac{k_BT}{E_F} \tag{C.94}$$

and for $T = 300$ K we find $\eta_{Cu} \approx 3.7 \cdot 10^{-3}$ and $\eta_{Na} \approx 8.0 \cdot 10^{-3}$.

6.11. The phonon contribution to the heat capacity given by Einstein is

$$C_v^{ph} = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2} \tag{C.95}$$

The other expressions can be found in the text book. The ratios asked for are given below.

T(K)	0.3	4	20	77	300
Ratio	117	0.65	0.026	0.0033	0.0064

From this it is clear that the electronic contribution to the heat capacity is important only at very low temperatures. Why does the ratio increase somewhat from 77 to 300 K?

6.12. The energies are

$f(E,T)$	0.5	0.7	0.9	0.95
E (eV)	5	4.98	4.94	4.92

Note that $f(E,T)$ rapidly approaches 1 for energies below the Fermi level.

6.13. The cyclotron frequency, ω_c, is given by the formula, $\omega_c = eB/m$, and $\omega_c = 2\pi f_c$ thus $B = \frac{2\pi f_c m}{e} \approx 0.86$ Tesla.

6.14. The electron contribution to the heat capacity is

$$C_v^{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}. \tag{C.96}$$

From the Debye model we find that the phonon contribution to the heat capacity is

$$C_v^{ph} = 9Nk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x-1)^2} \rightarrow \begin{cases} 3Nk_B & \text{då} \quad T \gg \theta_D \\ \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3 & \text{då} \quad T \ll \theta_D \end{cases} \tag{C.97}$$

$T_F = 6.36 \cdot 10^4$ K and $\theta_D = 225$ K for Ag. There are three intersections. The intersection at $T = 0$ K is trivial. The intersection at high temperature is unphysical, since $C_v^{el} = C_v^{ph}$ when

$$\frac{\pi^2}{2} N k_B \frac{T}{T_F} = 3Nk_B \;\rightarrow\; T = \frac{6}{\pi^2} T_F, \tag{C.98}$$

which gives $T = 3,87 \cdot 10^4$ K. This temperature is fare above the boiling point 2466 K of Ag. For the third intersection $C_v^{el} = C_v^{ph}$ when

$$\frac{\pi^2}{2} N k_B \frac{T}{T_F} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3 \;\rightarrow\; T = \sqrt{\frac{5\theta_D^3}{24\pi^2 T_F}}, \tag{C.99}$$

which gives $T = 1,94$ K. Thus the approximation is correct, since $T \ll \theta_D$.

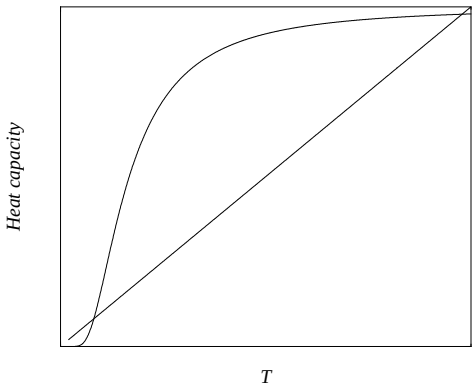

Figure C.8: The electron and phonon contributions to C_v.

7 Band Theory

7.1. A truly free electron is characterised by having a wave function $\psi_k = e^{i\mathbf{k}\cdot\mathbf{r}}$ and an energy $E_k = \frac{\hbar^2 k^2}{2m}$ with no restriction on the wave vector $\mathbf{k}$. If we assume a zero lattice (for simplicity in one dimension) with periodicity a we have also a Brillouin zone which restricts the wave vectors to be within the interval $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$. The free electron energy can, however, be displayed in the first BZ by suitable cutting and displacement of segments (addition or subtraction of reciprocal lattice vectors). This arrangement does not alter the physical situation but makes comparison with realistic situations easier. What differs a zero lattice from free space is the translational invariance assumed. Note that in free space all translations are symmetry operations. A zero lattice is often used to test codes of computer band structure programmes, because for a zero lattice you know the correct solution.

7.2. Band overlap cannot take place in one dimension as the BZ is also one-dimensional.

7.3. Do that.

7.4. We give here a general proof valid for all lattices. Applying periodic boundary conditions one obtains the k-vector density $\frac{V}{8\pi^3}$ where V is a volume that contains N cells and $V_{BZ} = \frac{8\pi^3}{V_C}$. Here V_{BZ} is the volume of the BZ and V_C the volume of the real space cell. The number of allowed k-states is the given by

$$\frac{V}{8\pi^3}\frac{8\pi^3}{V_C} = N. \tag{C.100}$$

7.5. Form problem 7.4 we have that the number of allowed k-states in one band is given by N. Since the electron spin can have two orientations the number of stater in one band is $n = 2N$.

7.6. The free electron energy is given by $E_k = \frac{\hbar^2 k^2}{2m}$. The energy ranges are obtained for $0 \leq k \leq \frac{\pi}{a}$, $\frac{\pi}{a} \leq k \leq \frac{2\pi}{a}$ and $\frac{2\pi}{a} \leq k \leq \frac{3\pi}{a}$ *i.e.* for the first three Brillouin zones.

7.7. The distance from the center of the BZ to one of the hexagonal faces is half of a primitive reciprocal lattice vector i. e. $\frac{\pi}{a}\sqrt{3}$, and with $\lambda = \frac{2\pi}{k}$ we obtain $\lambda = \frac{2a}{\sqrt{3}}$. Putting this into the Bragg law, $\frac{2a}{\sqrt{h^2+k^2+l^2}}\sin\theta = \lambda$, and noting that $\sin\theta = 1$ (normal incidence) we have

$$\frac{2a}{\sqrt{h^2+k^2+l^2}} = \frac{2a}{\sqrt{3}} \Rightarrow \text{(111)-planes.} \tag{C.101}$$

Similarly the distance from the center of the BZ to one of the square faces is $\frac{2\pi}{a}$ and reasoning in an analogous way as above we find that these faces are associated with reflections from the (200)-planes.

7.8. As for the BCC lattice the corresponding BZ has 12 faces. The distance from the center of the BZ to any of these faces is half of a primitive reciprocal lattice vector i. e. $\frac{\pi\sqrt{2}}{a}$. Proceeding in an analogous way as in problem 7.7 will show that these faces are associated with reflections from the (110)-planes.

7.9. The potential is periodic $\Rightarrow V(x) = \sum_G V_G e^{iGx}$ with Fourier expansion coefficients given by

$$V_G = \frac{1}{a}\int_{-a/2}^{a/2} V(x)e^{-iGx}dx = \frac{1}{a}\int_{-a/10}^{a/10} V_0 e^{-iGx}dx, \tag{C.102}$$

after integration we obtain

$$V_G = \frac{V_0}{5}\frac{\sin\frac{aG}{10}}{\frac{aG}{10}}. \tag{C.103}$$

Now $G = 0, \pm\frac{2\pi}{a}, \pm\frac{4\pi}{a}, \pm\frac{6\pi}{a}$ etc. and the gaps, E_g, are $E_g = 2|V_G|$. Thus we obtain

$$\begin{aligned} E_g^1 &= 2|V_{2\pi/a}| = \frac{2V_0}{\pi}\sin\frac{\pi}{5} \approx 0.374V_0 \text{ and analogously} \\ E_g^2 &= 2|V_{4\pi/a}| = \frac{V_0}{\pi}\sin\frac{2\pi}{5} \approx 0.303V_0 \text{ and} \\ E_g^3 &= 2|V_{6\pi/a}| = \frac{2V_0}{3\pi}\sin\frac{3\pi}{5} \approx 0.202V_0 \end{aligned}$$

for the first three gaps.

7.10. (a) Let the electrons be confined to a cube of edge L, and require periodic boundary conditions. Then we find that the components of the wave vector $\mathbf{k}$ must satisfy $k_x = 0; \pm 2\pi/L; \pm 4\pi/L; \ldots$ and similarly for k_y and k_z. From this we find a k-vector density $(2\pi/L)^3$. Since the Fermi sphere contains all N electrons we get

$$2\frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}k_F^3 = N, \tag{C.104}$$

where the factor 2 on the left comes from the two allowed spin quantum numbers. From this we find the desired result.

(b) The nearest distance from the center of the BZ to a surface is the distance to the hexagonal faces. From problem 7.7 we thus have that $k_{min} = \pi\sqrt{3}/a$. Denoting the number of valence electrons per atom with z and recalling that

the cubic cell of an FCC structure, with one atom per primitive cell, contains four atoms we have

$$\left(3\pi^2\frac{4z}{a^3}\right)^{1/3} = \frac{\pi\sqrt{3}}{a} \Rightarrow z = \frac{\pi\sqrt{3}}{4} \approx 1.36 \tag{C.105}$$

(c) Let N denote the total number of atoms, out of which N_1 is the number of Cu atoms. The average valence is then

$$\frac{N_1 \cdot 1 + (N - N_1) \cdot 2}{N} = z \tag{C.106}$$

from which we find $\frac{N_1}{N} = 2 - z = 0.64$. Thus 64 % Cu and 36 % Zn.

8 Semiconductors

8.1. The so-called bond model has its roots in quantum chemistry for analyses of electron structures of molecules. One simple example is the molecule CH_4 for which the tetrahedral symmetry is associated with the formation of covalent bonds. Transferred to covalent solids, like Si, a reasoning like that for answering problem 4.1 is generally attempted. The strength of this model is that it is easily grasped, gives some understanding of the bonding mechanism and easily illustrates the known fact that the electron density is largest in the region midway between nearest neighbours. However, for quantitative purposes this model is unsatisfactory. The electrons, are not actually localised to bonds. Like free electrons in a metal the wave functions extend throughout the crystal. This is clear from the statement of the Bloch theorem

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{C.107}$$

which is central in the band model. Having solved the Schrödinger equation $\hat{H}\psi_{nk}(\mathbf{r}) = E_{nk}\psi_{nk}(\mathbf{r})$ for a dense mesh of wave vectors within the 1st BZ, the electron density can be calculated from the formula

$$\rho(\mathbf{r}) = \sum_n \int_{BZ} \psi^*_{nk}(\mathbf{r})\psi_{nk}(\mathbf{r})d^3k, \tag{C.108}$$

where n is a sum over all bands occupied with electrons and the integration is over the 1st BZ. In agreement with the bond model this density is largest between nearest neighbours. However, much more quantitative information can be obtained from the solutions; such as effective masses, band gaps etc. In the bond model there is no way for instance to explain the difference between an indirect band gap and a direct one.

8.2. The bond orbitals correspond to the valence band. Usually the wave functions of the valence band are called "bonding" while the wave functions corresponding to the conduction band are called "antibonding".

8.3. If the wave functions are calculated for the conduction band one finds that the probability distribution is rather flat. Thus these electrons are more like free electrons than like electrons in covalent bonds.

8.4. A broken bond in the bond model corresponds to an excitation of an electron from the valence band to the conduction band.

8.5. Hall effect- and cyclotron resonance experiments show that the holes in the valence band behave as charge carriers. For this to be possible the electrons must be mobile.

8.6. No. Even a doped sample exhibits intrinsic behaviour if the temperature is high enough.

8.7. The Hall coefficient for a sample with holes and electrons i. e. two types of carriers is given by

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(n\mu_e + p\mu_h)^2}. \tag{C.109}$$

Putting $R_H = 0$ one finds that $\frac{p}{n} = \left(\frac{\mu_e}{\mu_h}\right)^2$. Taking Si as an example $\mu_e = 1300$ cm^2/Vs and $\mu_h = 500$ cm^2/Vs. This gives $\frac{p}{n} \approx 6.8$, meaning that the sample is weakly p - doped.

8.8. (a) Using $T = 300$ K, $E_g = 1.10$ eV and the relation

$$n_i = p_i = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} (m_e m_h)^{3/4} e^{-E_g/k_B T}, \tag{C.110}$$

we find that $n_i = p_i = 1.1 \cdot 10^{16}$ m^{-3}.

(b) From the relation

$$\mu = E_c + \frac{1}{2}E_g + \frac{3}{4}k_B T \ln\left(\frac{m_h}{m_e}\right) \tag{C.111}$$

we get $\mu = E_c + E_g/2 + 0.007$ eV.

8.9. (a) The atoms may be considered as hydrogen atoms in a dielectric surrounding. The energy levels of a hydrogen atom in vacuum are given by

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2}\frac{Z^2}{n^2} = 13.6\frac{Z^2}{n^2} \text{ eV}, \tag{C.112}$$

where Z is the effective charge of the atomic nucleus. In the dielectric surrounding ϵ_0 is changed to $\epsilon_r\epsilon_0$ and the mass m is changed to m^*m. The ionisation energy is equal to $|E_1|$, so we find $E_d = 13.6 \cdot 0.07/(13.13)^2 = 5.5$ meV, and $E_a = 13.6 \cdot 0.09/(13.13)^2 = 7.1$ meV.

(b) The radius of a hydrogen atom in its ground state is given by

$$r = \frac{h^2\epsilon_0}{\pi m e^2}\frac{1}{Z} = a_0\frac{1}{Z}, \tag{C.113}$$

where $a_0 = 0.53$ Å. This gives for the donors and acceptors that $r = \epsilon_r m a_0/m^*$, so we find $a_d = 99$ Å, $a_a = 77$ Å

(c) At sufficiently low temperatures the donors and acceptors are not ionised i. e. the holes and electrons are "frozen" at their impurity sites. The temperature at which freezing takes place can be estimated from the equation $E_d \approx k_B T$ which for the donor gives that $T = 64$ K. We can therefore always be sure that all donors and acceptors are ionised at room temperature.

8.10. (a) From problem 8.8 we have that $n_i = p_i = 1.1 \cdot 10^{16}$ m^{-3}. We see directly that this number is much smaller than the concentration supplied by the donors provided that they are ionised which always can be assumed at room temperature.

(b) From the law of mass action we have, $np = n_i^2$, but $n = N_d + p$ so $p^2 + pN_d - n_i^2 = 0$. Solving for p we obtain (note that $p > 0$)

$$p = -\frac{N_d}{2} + \sqrt{\left(\frac{N_d}{2}\right)^2 + n_i^2}. \tag{C.114}$$

Numerically we might find that $p = 0$, if this is the case we have to blame our pocket calculator. Instead of purchasing a new one we solve the equation

$$pN_d - n_i^2 = 0, \tag{C.115}$$

i. e. neglecting p^2 as it must be small. We then find that $p = 1.21 \cdot 10^9$ m^{-3} and $n = 1.0 \cdot 10^{23}$ m^{-3}. From the expressions in the text book for n and p an expression for the Fermi level can be obtained and be given by

$$\mu = E_c + \frac{E_g}{2} + \frac{k_B T}{2} \ln\left(\frac{n}{p}\right) + \frac{3}{4} k_B T \ln\left(\frac{m_h}{m_e}\right) \tag{C.116}$$

Numerically we find $\mu = E_c + E_g/2 + 0.421$ eV.

(c) If we introduce acceptors with a concentration of i $N_a = 6.0 \cdot 10^{21}$ m^{-3} we note that the sample above is still effectively n-doped with $N_d = 1.0 \cdot 10^{23} - 6.0 \cdot 10^{21} = 9.4 \cdot 10^{22}$ m^{-3}. Identical calculations as above shows a slightly lower value for the Fermi level.

8.11. (a) From the expressions for electron- and hole mobilities in the text book we obtain

$$\tau_e = \frac{m_e \mu_e}{e}, \quad \tau_h = \frac{m_h \mu_h}{e} \tag{C.117}$$

and numerically $\tau_e = 5.4 \cdot 10^{-13}$ s, $\tau_h = 2.7 \cdot 10^{-13}$ s.

(b) From problem 8.8 we have that $n_i = p_i = 1.1 \cdot 10^{16}$ m^{-3}, so we have that $\sigma_i = n_i e(\mu_e + \mu_h) = 3.2 \cdot 10^{-4}$ $(\Omega\text{m})^{-1}$.

8.12. From the text book we know that the Hall coefficient is given by

$$R_H = -\frac{1}{ne} = -\frac{E_y}{B_z J_x}, \tag{C.118}$$

from which we obtain that

$$n = \frac{B_z J_x}{e E_y}. \tag{C.119}$$

With reference to the Figure C.9 below we have

$$n = \frac{B_z I/bh}{eV_H/h} = \frac{B_z I}{ebV_H} = 4.7 \cdot 10^{21} \text{ m}^{-3}. \tag{C.120}$$

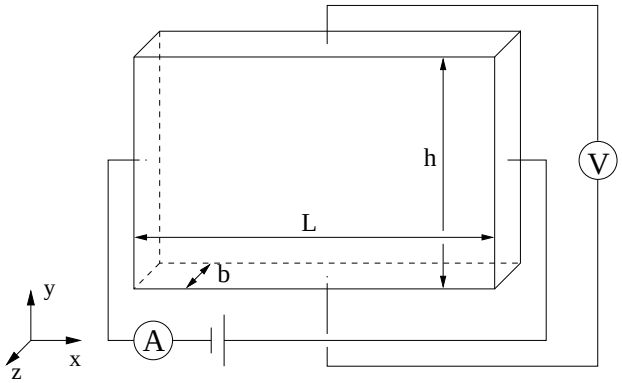

Figure C.9: The setup in a Hall experiment.

8.13. (a) The first equality in equation (C.118) directly yields that $R_H = -6.24 \cdot 10^{-4}$ m^3/As.

(b) Noting that $R_H = -\frac{E_y}{B_z J_x} = -\frac{V_H/h}{B_z I/bh}$ (see Fig.C.9) we have

$$V_H = -\frac{B_z I R_H}{b} = 3.74 \cdot 10^{-3} \text{ V}. \tag{C.121}$$

9 Superconductivity

9.1. The induced magnetic field on the surface of the wire must be lower than the critical field. The critical field is determined by

$$B_c(T) = B_c(0)\left(1 - \left(\frac{T}{T_c}\right)^2\right), \tag{C.122}$$

and the induced magnetic field is determined by *Biot-Savart formula*:

$$B = \frac{\mu_0}{4\pi}\frac{2I}{r}. \tag{C.123}$$

This gives $I = 54$ A for a wire of diameter 1 mm and a diameter 1.9 mm to carry a current of 100 A. This should be compared with a copper wire is a Swedish electrical installation, which if the area is 1.5 mm^2 only may hold a current of 10 A.

9.2. The inductance L of the solenoid is determined by

$$L = \mu_0 \frac{N^2 A}{l} = 38 \text{ mH} \tag{C.124}$$

The current is given by

$$I(t) = I_0 \exp\left(-\frac{Rt}{L}\right) \approx I_0\left(1 - \frac{Rt}{L}\right) \Rightarrow R = \frac{L}{t}\frac{I_0 - I(t)}{I_0}, \tag{C.125}$$

when Rt/L is small. From this one finds $R < 1.06 \cdot 10^{-14}$ Ω and $\rho < 6.0 \cdot 10^{-24}$ Ωm. Compare this with the resistivity of copper which is $1.70 \cdot 10^{-8}$ Ωm *i.e.* 15 orders of magnitude larger.

9.3. Use the relation

$$T_c = 1.14\theta_D \exp\left(\frac{-1}{UD'(\epsilon_F)}\right), \tag{C.126}$$

where U is the strength of the electron-lattice interaction and $D'(\epsilon_F)$ is the electron density of orbitals of *one spin* at the Fermi level. Also use the experimental value of γ to determine $D(\epsilon_F)$ by the relation

$$\gamma = \frac{1}{3}\pi^2 D(\epsilon_F) k_B^2, \tag{C.127}$$

where $D(\epsilon_F)$ is the density of states, *i.e.* two times larger than $D'(\epsilon_F)$ in the equation above.

	T_c (K)	θ_D (K)	γ (mJ/mol K^2)	$D(\epsilon_F)$ (eV^{-1} atom^{-1})	U (eV atom)
Al	1.140	428	1.35	0.5727	0.576
Pb	7.193	105	2.98	1.264	0.563

9.4. From a plot of $\ln(T_c)$ *vs.* $\ln(M)$ one find that $T_c \sim M^{-0.5}$, which is equal to what is predicted by the BCS theory.

9.5. Close-packing of the fluxoids meant that there is one quantum of flux $\Phi_0 = \pi\hbar/e$ in an area of $\sqrt{3}(2\xi)^2/2$. Thus $B_{c2} = 0.41$ T.

10 Optical and Dielectric Properties

10.1. In the free electron model the band structure consist of parabolic bands as

$$E_i(\mathbf{k}) = \frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{G}_i)^2, \tag{C.128}$$

where $\mathbf{G}_i$ are reciprocal lattice vectors. Potassium has BCC structure which means that the primitive G vectors are given by $\frac{2\pi}{a}(\pm\hat{x} \pm \hat{y})$. Optical excitation starts when the photon energy is high enough to lift an electron from the Fermi level to the closest unoccupied band, with the k-vector unchanged. Since K is a monovalent metal, the first band is not filled, so the excitation starts when electrons are taken from the first band,$|\mathbf{G}_0| = 0$ to the second band,$|\mathbf{G}_1| = \frac{2\pi\sqrt{2}}{a}$. Thus the threshold energy is obtained from

$$\hbar\nu = E_1(k_F) - E_0(k_F) = \frac{\hbar^2}{2m}|(k_F - G_1)^2 - k_F^2| = E_F\left|\left(\frac{k_F - G_1}{k_F}\right)^2 - 1\right|. \tag{C.129}$$

The free electron model give $k_F = (3\pi^2 N/V)^{1/3}$, and for a monovalent BCC metal $N/V = 2/a^3$, so $\hbar\nu = 0.61E_F = 1.29$ eV. Using the relation $E = \frac{hc}{\lambda}$, one finds that this energy corresponds to $\lambda = 959$ nm, *i.e.* infra red light.

10.2. The Clausius-Mossotti relation is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{1}{3\epsilon_0}\sum n_i\alpha_i, \tag{C.130}$$

where n_i is the concentration and α_i is the polarisability of atom i. The refractive index is given by $n^2 = \epsilon$.

NaCl has FCC structure with $a = 5.63$ Å, so $\sum n_i\alpha_i/3\epsilon_0 \approx 0.303$, which give $n = 1.52$.

CsCl has SC structure with $a = 4.11$ Å, so $\sum n_i\alpha_i/3\epsilon_0 \approx 0.343$, which give $n = 1.60$.

10.3. See the figure in chapter 13 in Kittel.

10.4. The force on the electron due to the nucleus is

$$F = \frac{-e^2}{4\pi\epsilon_0 r^2}\hat{r}, \tag{C.131}$$

if the origin is at the nucleus. The polarisability α is defined by $\mathbf{p} = \alpha\mathbf{E}_{local}$, where $\mathbf{p}$ is the electric dipole moment $\mathbf{p} = e\mathbf{x}$. The requrement that the x-component of the force from the nucleus and the force from the electrical field must be equal in magnitude give

$$\frac{e^2}{4\pi\epsilon_0 r^2}\frac{x}{r} = eE. \tag{C.132}$$

If $x \ll a_H$ we get

$$p = \frac{e^2 E 4\pi\epsilon_0 a_H^3}{e^2}, \tag{C.133}$$

so the polarisability can be identified to be $\alpha = 4\pi\epsilon_0 a_H^3$.

10.5. Let the local electrical field be given by $E_{local} = E_0 \sin\omega t$. Then the equation of motion is given by

$$m\frac{d^2x}{dt^2} + m\omega_0^2 x = -eE_0 \sin\omega t, \tag{C.134}$$

so that for $x = x_0 \sin\omega t$, one find

$$m(-\omega^2 + \omega_0^2)x_0 = -eE_0. \tag{C.135}$$

The dipole moment has the amplitude

$$p_0 = -ex_0 = \frac{e^2 E_0}{m(\omega_0^2 - \omega^2)} \Rightarrow \alpha = \frac{e^2/m}{\omega_0^2 - \omega^2}. \tag{C.136}$$

11 Magnetic Properties

11.1. The Langevin formula is

$$\chi_m = -\frac{\mu_0 N Z e^2}{6nV} < r^2 >, \tag{C.137}$$

where $\frac{N}{V} = \frac{N_A\rho}{M}$. The molar susceptibility is $\chi_m^{molar} = \frac{\chi_m M}{\rho}$ and the expectation value $< r^2 >$ is

$$< r^2 >= \int \psi^* r^2 \psi d^3r = -\frac{1}{\pi a^3}\int_0^\infty r^2 e^{-2r/a} 4\pi r^2 dr = 4a^2\int_0^\infty e^{-2x}x^4 dx = 3a^2, \tag{C.138}$$

so

$$\chi_m^{molar} = -\frac{N_A\mu_0 e^2 a^2}{2m} = -3.0\cdot 10^{-8}\ \mathrm{m^3/kmol} \tag{C.139}$$

11.2. The Hund rules affirm that electrons will occupy orbitals in such a way that the ground state is characterised by

- The maximum value of the total spin S allowed by the exclusion principle.
- The maximum value of the orbital angular momentum L consistent with this value of S
- The value of the total angular momentum J is
  - equal to $|L - S|$ if the shell is less than half full
  - equal to $L + S$ when the shell is more than half full
  - equal to S when the shell is half full, since then the first rule give $L = 0$

From this one find

	m_l								
	-3	-2	-1	0	1	2	3	S	L
Eu^{++} $(4f^7)$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$S = 7/2$	$L = 0$
Yb^{3+} $(4f^{13})$	$\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$S = 1/2$	$L = 3$
Tb^{3+} $(4f^8)$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$	$S = 3$	$L = 3$

and if one uses the symbolic notation $^{2S+1}L_J$ for the atomic state one find that the ground states are given by:

- Eu^{++}: $4f^7 5s^2 p^6 \quad {}^8S_{7/2}$
- Yb^{3+}: $4f^{13} 5s^2 p^6 \quad {}^2F_{7/2}$
- Tb^{3+}: $4f^8 5s^2 p^6 \quad {}^7F_6$

and calculating the effective number of Bohr magnetons by $p = g\sqrt{J(J+1)}$, where g is given by the Lande' equation

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}, \tag{C.140}$$

give (a) $p = 7.94$, (b) $p = 4.54$, and (c) $p = 9.72$.

11.3. (a) If the diamagnetic sample contain a paramagnetic contamination there will be a temperature dependent contribution to the total magnetic susceptibility. This paramagnetic is determined by the Curie law $\chi_{para} = C/T$. Thus the total magnetic susceptibility must be given by

$$\chi = \chi_{dia} + \chi_{para} = \chi_{dia} + \frac{C}{T}. \tag{C.141}$$

If χ is plotted *vs.* $1/T$, it is confirmed that there is a paramagnetic contribution to the total magnetic susceptibility.

(b) The Curie constant is given by

$$C = \frac{\mu_0 n p^2 \mu_B^2}{3k_B}, \tag{C.142}$$

where p is the effective number of Bohr magnetons. From the Hund rules one find that Mn^{2+}, with the configuration $3d^5$, has $S = \frac{5}{2}$, $L = 0$, and $J = S = \frac{5}{2}$, so the Lande' g-factor is $g = 2$. From the plot one find that the slope, which is equal to the Curie constant is $C = 1.90 \cdot 10^{-4}$ K. This give $n = 2.1 \cdot 10^{24}$ m^{-3}.

(c) The intercept in the plot is equal to the diamagnetic susceptibility and is found to be $\chi_{dia} = -9.53 \cdot 10^{-6}$.

11.4. The concentration of Fe^{3+} ions is $n = 9.3 \cdot 10^{27}$ m^{-3}. Fe^{3+} has the configuration $3d^5$ so the Hund rules give the ground state $^6S_{5/2}$, with $L = 0$ and $J = S = \frac{5}{2}$. If all the spins are parallel, then $S_z = 5/2$, which give the maximal magnetisation as $M_{max} = ng\mu_B S_z = 4.32 \cdot 10^5$ A/m.

11.5. (a) In the first turn the force on the weighting-machine is given by $F_1 = gV\rho_{salt}$. In the second turn there will be two additional forces. One, F_m, from the magnetic field as $F_m = V\chi H\frac{\partial B}{\partial z}$ and one due to the Archimedes' principle, $F_A = gV\rho_N$, where ρ_N is the density of liquid nitrogen. Thus the total force, F_2, in the second case is

$$F_2 = F_1 - F_A + V\chi H\frac{\partial B}{\partial z}, \tag{C.143}$$

where C is the Curie constant $C = \frac{\mu_0 n p^2 \mu_B^2}{3k_B}$. This give $p = 3.85$.

(b) Theoretically Cr^{3+} with the configuration $3d^3$ has $S = 3/2$. Since Cr is a iron group ion, the effective number of Bohr magnetons is given by $p = g\sqrt{S(S+1)} = 3.87$.

11.6. The spontaneous magnetisation is determined by

$$M = n\mu_B \tanh\left(\frac{\mu_0\mu_B\lambda M}{k_B T}\right). \tag{C.144}$$

Introduce the reduced magnetisation $m = M/n\mu_B$ and the reduced temperature $t = T/T_c$, where $T_c = n\mu_0\mu_B^2\lambda/k_B$, so that $m = \tanh(m/t)$ or $t = \frac{m}{\tanh^{-1}(m)}$. An expansion of $\tanh^{-1}(m)$ as $m + m^3/3 + ...$, when $m \to 0$ at the Curie point give

$$t = \frac{m}{\tanh^{-1}(m)} \approx \frac{m}{m + m^3/3} \approx 1 - \frac{m^2}{3} \tag{C.145}$$

so

$$m^2 = 3(1-t) = 3\frac{T_c - T}{T_c} \Rightarrow m \sim (T_c - T)^{1/2}. \tag{C.146}$$

D

Lab: X – Ray Crystallography

1 Purpose

The purpose of this lab session is to introduce you to some simple laboratory work to determine the crystal structures of some unknown samples. You will perform a measurement of a set of powders. After you are finished you will analyse the scattering pattern. You will determine the crystal structure and the lattice constant.

The central piece of equipment in this lab session is a Tel–X–Ometer made by TELTRON. It carries the X–ray generating equipment and also the mechanical system to carry a Geiger–Müller tube. In principle it is a Debye–Scherrer camera but instead of film we use a Geiger–Müller tube to pick up the signal.

2 Literature

C. Kittel, Introduction to Solid State Physics, chapter 1 and 2,
J.R. Hook and H.E. Hall, Solid State Physics: chapter 4 and 11.

3 X–ray diffraction, some general principles

3.1 Bragg law

To investigate crystals with X–rays it is important that the wavelength λ of the X–rays is of the same order as the separation between the atoms. The relation between λ in Ångström (Å) and the X–ray photon energy E in keV is given by

$$\lambda(\text{Å}) = \frac{12.4}{E(\text{keV})} \tag{D.1}$$

For a wave length in the range of 1 Å, required for crystal investigations, the photon energy has to be in the keV range. Instead of X–rays one may also use electrons or neutrons in crystallography, the appropriate energies will however be different, 100 eV and 0.01 eV respectively (see CK page 28 figure 1).

The geometrical conditions for diffraction are the same irrespective of if one uses X–rays, electrons or neutrons. They differ however greatly in other respects like absorption and scattering. X–rays and neutrons are appropriate if we wish to investigate the inner

parts of a crystal as they are not strongly absorbed. Electrons interact strongly with the electrons of the crystal, and hence they are more suitable for investigations of surface effects and thin films (see CK page 560 figure 5).

The physical process that gives rise to the diffraction of the X–rays is the interaction of the X–ray with the electrons of the crystal. The electromagnetic field of the incident X–ray photons accelerate the electrons, and they will oscillate with the field. The oscillating electrons emit electromagnetic radiation with the same frequency as the incident X–rays. The emitted radiation from different atoms can give rise to positive interference. This we see as a reflected beam.

The geometrical diffraction condition (see CK page 29), **Bragg's law**

$$2\mathrm{d}\sin(\theta) = \mathrm{n}\lambda \qquad \text{(n: 1,2,3,... gives the order of the reflection)} \qquad \text{(D.2)}$$

is simple to deduce (figure D.1). The relation eq. (D.2) shows that we will only have a reflected beam for certain values of θ, for an ordinary mirror any θ will do. The reflected

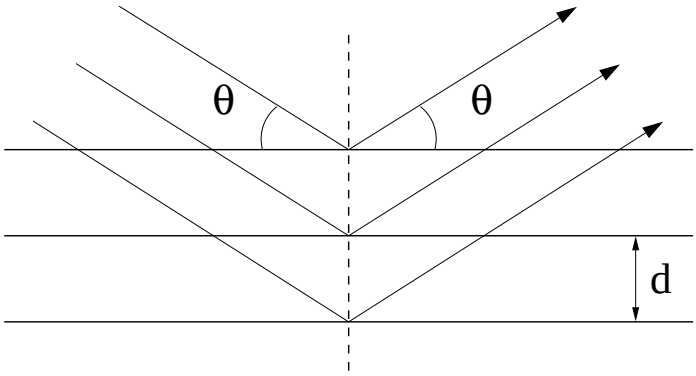

Figure D.1: Reflection according to Braggs law

beam consists of reflections from many partially reflecting planes that in certain directions perform a constructive interference. We also see that the wave length must satisfy the condition $\lambda \leq 2\mathrm{d}$ which implies that ordinary light cannot be used for the study of crystal structures, as the separation d between planes is in the range of a few Å. As can be seen

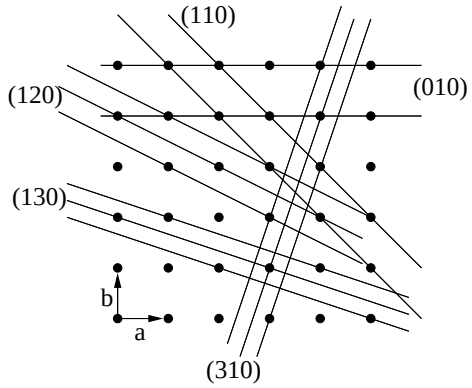

Figure D.2: Examples of some reflecting planes with Miller indices.

from figure D.2 there are many ways to form a set of parallel planes suitable for reflections.

The distance d(hkl) between parallel planes is a function of the Miller – indices (hkl) (see section below) that characterise different sets of parallel planes.

In the example in figure 2 we have a simple crystal structure consisting of a simple square lattice with a basis of just one atom. With a more complicated basis we will get reflections from all atoms in the basis. So what will we see? As every atom in the basis is a member of a point lattice with the same properties as the crystal lattice, the atoms in the basis will not change (=add more) the allowed Bragg reflections of the crystal lattice.

One can regard the crystal as consisting of a set of point lattices, one for each atom in the basis. All these point lattices have the same structure as the crystal lattice and they are offset to each other according to positions of the atoms in the basis. We see that all the point lattices have the same Bragg condition for reflection as the crystal lattice. As the different point lattices are offset from each other a reflection from one point lattice will be out of phase with the same reflection for another point lattice. It might even be so that the reflection from one point lattice is one half wave length out phase with that from another point lattice. In this case they will interfere destructively and fully extinguish each other and one of the Bragg reflections of the crystal lattice will be missing (if there are more point lattices the situation becomes more complicated).

Concluding. For a crystal structure the possible directions are given by the crystal lattice. The atoms of the basis only affect the intensity of the different reflections, and some reflections might even disappear.

A consequence of this is that a determination of the diffraction angles θ will only alow us to determine the crystal lattice but will not help us to determine the basis. To do anything on the basis like determine the positions of the atoms, we need to study the intensities of the Bragg reflections as well. So it is quite a difficult task to determine the structure of the unit cell, both theoretically and experimentally, as there are no simple and general rules.

3.2 Miller indices

The orientation of a plane in a lattice is specified by giving its *Miller indices*, which are defined as follows: To determine the indices of the plane P in figure D.3, we find its intercepts with the axes along the basis vectors **a, b,** and **c**. Let these intercepts be *x, y,*

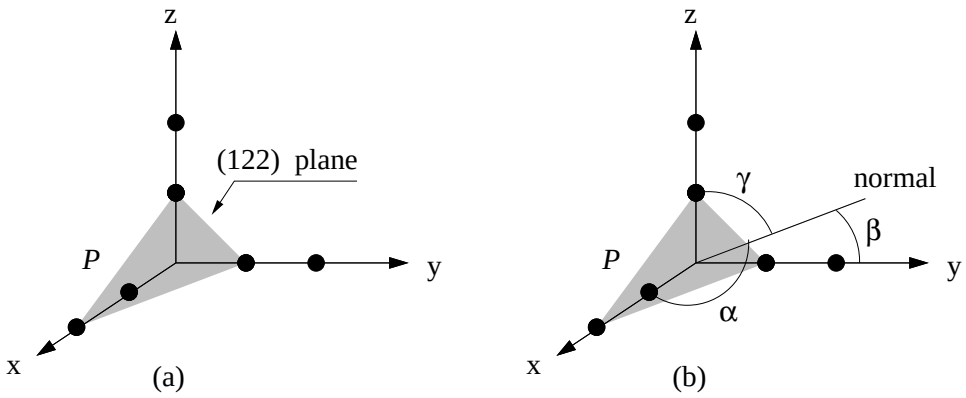

Figure D.3: (a) The (122) plane. Solid circles show the lattice points

and *z*. Usually x is a fractional multiple of a, y a fractional multiple of b, and so forth.

We form the triplet

$$\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right), \tag{D.3}$$

invert it to obtain the triplet

$$\left(\frac{a}{x}, \frac{b}{y}, \frac{c}{z}\right), \tag{D.4}$$

and then reduce this set to a similar one having the smallest integers by multiplying by a common factor. This last set is called the *Miller indices* of the plane and is indicated by (hkl). Let us make an example: Suppose that the intercepts are $x = 2a, y = \frac{3}{2}b$, and $z = 1c$. We first form the set

$$\left[\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right] = (2, \frac{3}{2}, 1), \tag{D.5}$$

then invert it $\frac{1}{2}, \frac{2}{3}, 1$ and finally multiply by the common denominator, which is 6, to obtain the Miller indices (346) (pronounced as "three four six").

We note that the Miller Indices are so defined that all equivalent, parallel planes are represented by the same set of indices. Thus the planes whose intercepts are $x, y, z; 2x, 2y, 2z; -3x, -3y, -3z$; etc., are all represented by the same set of Miller indices. Therefore a set of Miller indices specifies not just one plane, but an infinite set of equivalent planes, as indicated in figure D.2. There is a good reason for using such notation, as will be evident from the study of X–ray diffraction from crystal lattices. A diffracted beam is the result of scattering from large numbers of equivalent parallel planes, which act collectively to diffract the beam.

The reason for inverting the intercepts in defining the the Miller indices is more subtle, and has to do with the fact that the most concise, and mathematically convenient, method of representing lattice planes is by using the so–called reciprocal lattice.

3.3 Spacing between planes of the same Miller indices.

In connection with x–ray diffraction from a crystal, one needs to know the inter–planar distance between planes labelled by the same Miller indices, say (hkl). Let us call this distance d_{hkl}. The actual formula depends on the crystal structure, and we confine ourselves to the case in which the axes are orthogonal. We can calculate this by referring to figure D.3 visualising another plane parallel to the one shown and passing through the origin. The distance between these planes ,d_{hkl}, is simply the length of the normal line drawn from the origin to the plane shown. Suppose that the angles which the normal line makes with the axes are α, β, and γ, and that the intercepts of the plane (hkl) with the axes are x, y, and z. Then it is evident from the figure that

$$d_{hkl} = x\cos\alpha = y\cos\beta = z\cos\gamma. \tag{D.6}$$

But there is a relation between the directional cosines $\cos\alpha, \cos\beta$, and $\cos\gamma$. That is $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$. If we solve for $\cos\alpha, \cos\beta$, and $\cos\gamma$ from the previous equation, substitute into the one immediately above, and solve for d_{hkl} in terms of x, y, and z, we find that

$$d_{hkl} = \frac{1}{\sqrt{\frac{1}{x^2} + \frac{1}{y^2} + \frac{1}{z^2}}} \tag{D.7}$$

Now x, y, and z are related to the Miller indices h, k, and l. If one reviews the process of defining these indices, one readily obtains the relations

$$h = n\frac{a}{x}, \quad k = n\frac{b}{y}, \quad l = n\frac{c}{z}, \tag{D.8}$$

where n is the common factor used to reduce the indices to the smallest integers possible. Solving for x, y, and z from eq. (D.8) and substituting into eq. (D.7) one obtains

$$d_{hkl} = \frac{n}{\sqrt{\frac{h^2}{x^2} + \frac{k^2}{y^2} + \frac{l^2}{z^2}}} \tag{D.9}$$

which is the required formula. Thus the inter–planar distance of the (111) planes in a simple cubic is $d = na\sqrt{3}$, where a is the cubic edge.

4 Diffraction conditions

4.1 Reciprocal lattice

To discuss the connection between the intensity of the scattered light and the properties of the unit cell it is necessary to take the distribution of the electrons in the unit cell into account (CK, page 30ff, HH 11.2). A calculation of the so called scattering amplitude (CK, page 34 eq. (18)) is done, which determines the intensity of the scattered light.

In a description of diffraction we introduce a **reciprocal lattice** and a **scattering vector** $\mathbf{\Delta k} = \mathbf{k}' - \mathbf{k}$, where $\mathbf{k}$ is the wave vector of the incident beam and $\mathbf{k}'$ is the wave vector of the scattered beam. We can now write the condition for diffraction

$$\mathbf{G} = \mathbf{\Delta k} \qquad \text{(CK, page 35, eq. (21))} \tag{D.10}$$

which is equivalent to Braggs law. $\mathbf{G}$ is a vector of the reciprocal lattice. We will commit ourselves only to cubic lattices (sc, fcc, or bcc). As we analyse our diffraction data we will always use a description based on a simple cubic lattice (sc). Hence also the reciprocal lattice is a simple cubic lattice. Let $\mathbf{b}_1, \mathbf{b}_2$, and $\mathbf{b}_3$ be the primitive basis vectors of the reciprocal lattice, we can then write $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$. Every reflected beam can according to eq. (D.10) be connected to a reciprocal lattice vector, ie characterised by three integers h, k and l.

Problem 1 Show the following: Study the scalar product between $\mathbf{G}$ and a vector $\mathbf{R}$ in the direct lattice (sc) and show:
That every shortest reciprocal lattice vector in a certain direction (ie the integers h, k, and l do not contain a common factor) is perpendicular to a set of lattice planes in the direct lattice.

The distance between two proximate planes is in the direct lattice given by $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$. If the integers h, k and l contain a common factor m, (hkl) = (mh'mk'ml'), then the separation between the (hkl) planes is only a factor of 1/m to the separation between the (h'k'l') planes. A first order reflection from the planes (hkl) planes corresponds to a

m–th order reflection from the (h'k'l') planes. As d(h'k'l') = md(hkl) we can write Braggs law

$$2\frac{\mathrm{d(h'k'l')}}{\mathrm{m}}\sin(\theta) = \lambda \qquad \rightarrow \qquad 2\mathrm{d(hkl)}\sin(\theta) = \lambda \tag{D.11}$$

and the order of the reflections does not appear explicitely in Braggs law anymore but only implicitly through a common factor in the integers h, k and l.

The diffraction condition gives that the scattering amplitude of a crystal with a unit cell containing more than one atom will contain a factor

$$S(hkl) = \sum_j f_j e^{-i2\pi(hx_j+ky_j+lz_j)} \qquad \text{(CK, page 44, eq. (46))} \tag{D.12}$$

S(hkl) is called the **structure factor** and the f_j are called the **atomic scattering factor** or also sometimes **atomic form factor**. The size of $\mid S(hkl) \mid$ is the amplitude of the scattered beam from the unit cell and its argument gives the phase difference between the scattered wave compared to if the wave had been scattered by an electron at the origin.

4.2 The structure factor of some cubic lattices

The principles are given in CK page 44 – 45, where also a calculation of the structure factor of a bcc– and fcc– structure is done. Here we will start of with the calculation of the structure factor of the NaCl structure.

The unit cell contains 4 Na^+ – ions and 4 Cl^- – ions with the following coordinates:

$$\mathrm{Na^+} : (0,0,0), \left(\frac{1}{2},\frac{1}{2},0\right), \left(\frac{1}{2},0,\frac{1}{2}\right), \left(0,\frac{1}{2},\frac{1}{2}\right) \tag{D.13}$$

$$\mathrm{Cl^-} : \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) \left(0,0,\frac{1}{2}\right) \left(0,\frac{1}{2},0\right) \left(\frac{1}{2},0,0\right) \tag{D.14}$$

$$S = \left[f_{\mathrm{Na^+}} + f_{\mathrm{Cl^-}} e^{-i\pi(h+k+l)}\right] X \left[1 + e^{-i\pi(h+k)} + e^{-i\pi(h+l)} + e^{-i\pi(k+l)}\right] \tag{D.15}$$

where the reciprocal lattice vector **G** is characterised by the Miller indices h, k, and l.

The second parenthesis gives the condition for destructive interference of the fcc lattice. The first parenthesis shows that, as $f_{\mathrm{Na^+}} \neq f_{\mathrm{Cl^-}}$, the intensities of the maxima where (h+k+l) is an even number will be larger compared to the ones where (h+k+l) is an odd number.

$$\begin{aligned} \mathrm{S} &= 0, \text{ if (hkl) is mixed of odd and even numbers.} \\ &= \left(f_{\mathrm{Na^+}} + f_{\mathrm{Cl^-}}\right), \text{ if (hkl) are even numbers.} \\ &= \left(f_{\mathrm{Na^+}} - f_{\mathrm{Cl^-}}\right), \text{ if (hkl) are odd numbers.} \end{aligned}$$

Problem 2 Calculate the structure factors for the CsCl structure and for the diamond structure.

5 Equipment and safety

5.1 X–ray equipment and safety

At the lab site there is a more thorough description of the equipment. You can find this on a lead attached to the X–ray equipment. As we all know X–rays are dangerous. Never try to run the X–ray generator without the lid in it's proper position ie. closed. In figure D.4 you see an overall picture of the equipment a Tel–X–Ometer made by TELTRON. Start

Figure D.4: The Tel–X–Ometer.

by having a look at the Tel–X–Ometer. A prominent feature is the plastic lid (radiation cover). It covers the spectrometer table. In this area the experiment is made. In the centre of the spectrometer table the sample under investigations is mounted. From the centre an arm carrying the Geiger–Müller tube figure D.5 reaches out under the radiation

Figure D.5: The Geiger–Müller tube.

cover. As you move the arm along the perimeter of the spectrometer table you see that

the sample holder in the centre also rotates but at *half* the angular rotation of the arm. The X–rays are generated by a miniature X–ray tube (see figure D.6), that is the small (size of medium sized apple) glass dome 'sitting' on the spectrometer table. You open the

Figure D.6: The miniature X–ray tube.

lid (radiation cover), in the following way: Let the metal part with the international sign for radiation point towards you. The lid can be moved sideways either to the left or to the right the appropriate directions is towards the side of the Geiger–Müller tube. If moved in the opposite direction the lid will jam the rotating arm carrying the Geiger–Müller tube, see figure D.5. The lid seems to be made out of some simple plastic but when closed hardly no X–rays can escape from the Tel–X–Ometer. The plastic it is made of has a high content of Chlorine and absorbs scattered radiation. The beam in itself (the non scattered part) is stopped by the metal part of the lid. The metal part bears the international symbol for radiation. The outside diameter of the three foil represents the maximum diameter of the un collimated X–ray beam.

The lid also operates a safety switch to prevent the X–ray generator from operating while the lid is open. The plastic lid cover the upper area of the equipment this part is called the spectrometer table. In figure D.7 you see the two switches to operate the

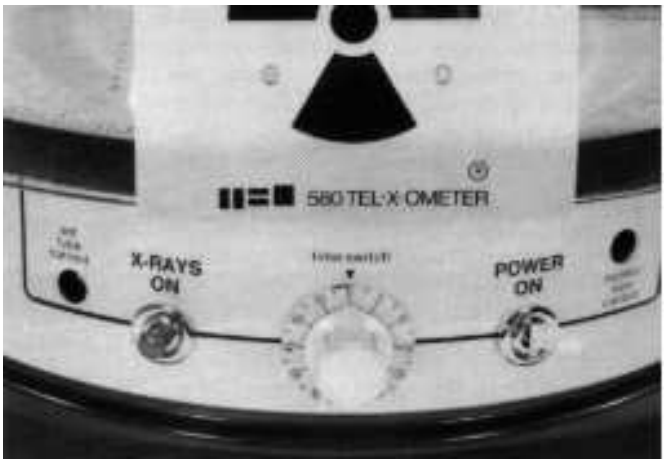

Figure D.7: Operating controls of the Tel–X–Ometer.

power. The right one turns the power on but X–rays re not generated yet. This you do

by turning the left switch on. In between the two switches you see a timer. You have to set the timer to some appropriate time if it runs out of time the X–ray source will be turned of. This is not only a safety precaution but also saves the X–ray tube as it only has a limited lifetime. Your operations of the switches are confirmed by the two lamps (see figure D.8) on top of the spectrometer table one white to indicate the power on switch

Figure D.8: Indication lamps on the Tel–X–Ometer.

and one red to indicate that the X–ray tube is operating.

5.2 The Geiger–Müller counter

Several years ago one used film to record the X–ray diffraction pattern in a Debye–Scherrer camera. In the experiment you will do we will not use film but we will use a Geiger–Müller counter. It makes operation of the experiment simpler as we do not have to handle film anymore. As you are familiar with the operation of the physical processes in a G–M tube I will not mention them here. I will now describe how to operate the counter figure D.9. Turn it on by pushing the power button. It first initiates itself displaying 'r 1.0', after a while a zero appears and the apparatus is ready. The lamp Manual is on continuously and the lamp Memory is on intermittently. In principle the apparatus is now ready for manual measurement. But lets be a bit more sophisticated. Now we have to set it for our purpose.

1. *Firstly* you have to adjust the G–M voltage. Push the 'select' button several times until the lamp G–M voltage lights up intermittently, now push 'enter', the G–M voltage lamp is on continuously. In the display window you see the voltage, it should be 405 – 415 Volts, if not adjust with the knob to the far left. When satisfied (or if correct) with adjustments you push 'enter' again and the G–M voltage lamp lights up intermittently again.

2. *Sound* Push the 'select' button several times til the sound lamp lights up intermittently, push 'enter', now the sound lamp is on continuously. Pushing the 'select'

Figure D.9: The control unit of the Geiger–Müller tube.

button you can either turn the sound on or off. Status is shown in the display window. When satisfied confirm with pushing the 'enter' button and the sound lamp lights up intermittently again.

3. *Start measuring* Push the 'select' button several times til the lamp 'GATE' lights up intermittently. Press 'enter', now a lamp inside the 'count period' lights up intermittently. Use the 'select' button again to choose a different time. Take 60 or 100 sec. Confirm with 'enter' and now the lamp continuous is on intermittently, use the 'select' button to pass by this one. Now it is set for measurement and you should not touch the 'select' or 'enter' buttons any more. If you do, you will have to go back to 'GATE' and reenter your selections.

   Start measurements by pushing the 'start' button. It starts counting and displays the number of counts made during 60 (or 100) seconds. To start a new measurement you will have to push the 'start' button again.

   The appropriate values for 2θ start at $\approx 18^o$ and increase to 90^o in steps of one degree. If you locate a peak investigate it more carefully in steps of 0.5^o

   While the counter is operating the select/enter buttons are inoperable. To stop the counter, either push stop or power of.

6 Calculations and lab work

At the lab site you find the TELTRON equipment prepared with a single crystal sample. These single crystals have all an FCC structure. Note the colour code (blue, red, green or yellow) on top of the crystal and write it down. Please do not try to change the crystal it might break.

You have also received 2 diffraction patterns made for two powder samples.

All these materials have cubic structures, ie sc, fcc, bcc, diamond, CsCl or ZnS.

You are going to determine the crystal structure for the two unknown powder samples.

The single crystal sample you measure yourselves using the ready to go TELTRON equipment. The crystal is mounted in the following way: The reflections you will see are like (100), (200), (300) etc. . So you will only see a fraction of the lines you would see

if it had been a powder as the crystal has a fixed orientation. The reason we make a measurement on a crystal is that the X-ray source of the TELTRON is weak. In a powder we have many small crystals randomly oriented so only a small fraction will be properly lined up for a reflection, whereas in the large single crystal a large volume of the crystal will give a reflection down into the GM tube.

Experimental task: In this lab you will be asked to do the following. From the two given powder diffraction patterns you have to determine the crystal lattice and the lattice constant a. From the experimentally (with the Teltron equipment) determined diffraction pattern of the single crystal you have to determine the lattice constant a, you cannot determine the crystal structure of this unknown crystal. But let's start with an example to get an idea of how the procedure works.

7 Crystal structure

From the experimentally determined θ–values calculate the corresponding for the separations between sets of lattice planes. As the x–rays mainly consist of two wave–lengths $K_{\alpha 1}$ and $K_{\alpha 2}$, use a weighted average value for the wave–length. Weighted with respect to their intensities.

The wave–length λ of the two K α photons of a Copper anode are : $K_{\alpha 1} = 1.540600$Å and $K_{\alpha 2} = 1.544390$Å. Use an average value in your calculations.

Order the calculated values for the separations d between lattice planes in a descending list. From this list you can determine the crystal structure by investigating how the observed values correspond to theoretically determined values for the different lattice structures. For cubic structures we have

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}.$$

or

$$\left(\frac{d_{hkl}}{a}\right)^2 = \frac{1}{h^2 + k^2 + l^2}. \tag{D.16}$$

As h,k, and l are integers so is also $h^2 + k^2 + l^2$. Hence the experimentally determined values for d^2/a^2 all have to correspond to inverted integers. By trial and error you determine these integers. We also have at hand the theoretically determined integers for the different structures. Lets give an example of the principle.

For a material whose structure we are to determine the following d values have been measured and calculated ($d = \lambda/2\sin\theta$).:

d	2.06	1.26	1.08	0.89	0.82	Å

Now we have to find the integers ($h^2 + k^2 + l^2$) that according to eq. (D.16) correspond to the experimental d–values above.

With an ordinary pocket calculator you can quickly establish the number x to multiply onto all the $1/d^2$ values to make them into a series of integers.

d	2.06	1.26	1.08	0.89	0.82
$1/d^2$	0.2356	0.6299	0.8573	1.2625	1.4872
x=2/0.2356 gives:	2	5.35	7.28	10.72	12.62
x=3/0.2356 gives:	3	8.02	10.92	16.08	18.94
Integers:	3	8	11	16	19

We have now to compare these 'experimental' integers with the theoretical ones given below:

$h^2 + k^2 + l^2$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
sc	x	x	x	x	x	x		x	x	x	x	x	x	x		x	x	x	x	x
fcc			x	x				x			x	x				x			x	x
bcc		x		x		x		x		x		x		x		x		x		x
diamond			x					x			x					x			x	

Values of $h^2 + k^2 + l^2$ for which $S \neq 0$, for some cubical structures.

.

By studying our experimental integers and comparing it to the table above we find that the only cubical structure that fits is the diamond structure.
From the structure factor for the diamond structure you have calculated earlier you can obtain the following table for (hkl) and $h^2 + k^2 + l^2$.

(hkl)	111	220	311	400	331	422	511	333
$h^2 + k^2 + l^2$	3	8	11	16	19	24	27	27

To determine the crystal structure of an unknown crystal we have to use the structure factor to determine the possible (hkl) that might occur.

Problem 3 Calculate a similar table as the above one for the diamond structure for the sc, fcc and bcc structures.

A determination of the NaCl– and CsCl–structures is done by a careful study of the intensities of the lines as well. As the structure factor S usually dominates the intensities we can study it approximately from the intensities.

Problem 4 Present the analysis of your results (see experimental task above) in the form of a table representing the values for θ, d, $h^2 + k^2 + l^2$, (hkl). Also give the result of your analysis regarding the structure and lattice constant a.

Lab–report
Your lab–report should contain answers to all problems 1–4.

8 Credits

This material has evolved from a similar lab session developed by Günter Grossman, Department of Solid State Physics, Lund University.

E

Lab: Electrons in periodic potentials, Band structure of crystals

Note You are expected to produce an answer to the part of the lab that is marked P1 on pages 5 and 6. The parts P2, C3,...C8 are excluded. These parts are based on perturbation theory and this has not been covered in the quantum mechanics course you have had.

1 Purpose

The purpose of this computer project is to give a knowledge about some of the basic properties of electrons in a crystal. You will also make use of newly acquired knowledge on perturbation calculations and the matrix representation. If you feel like refreshing your knowledge on perturbation theory please use the appendix you find at the end.
Keywords: reciprocal lattice, Bloch–states, Bloch–vector, Brillouin zone, band gap, effective mass.

2 Literature

C. Kittel, Introduction to Solid State Physics, chapter 6 and 7,
J.R. Hook and H.E. Hall, Solid State Physics: chapter 4 and 11.
Also required is knowledge of time independent perturbation calculations.

3 Background

In a macroscopic crystal there are approximately 10^{23} atoms and even more electrons. Each individual electron senses the attractive potential from the nuclei and the repulsive potential from other electrons. Also different nuclei repel each other. To solve the complete Schrödinger–equation (S–E) describing this complex many body system is an unsurmountable task. As an illustration lets write down the Hamiltonian for this many

body system consisting of N electrons and M nuclei (not taking spin into account):

$$\mathbf{H} = \underbrace{-\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{\alpha=1}^{M}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2}_{\text{electron and nuclear kinetic energy}} + \underbrace{\sum_{i<j}^{N}\frac{e^2}{\mid \mathbf{r}_i - \mathbf{r}_j \mid}}_{\text{electron–electron interaction}}$$
$$- \underbrace{\sum_{i=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{\mid \mathbf{r}_i - \mathbf{R}_\alpha \mid}}_{\text{electron–nuclear interaction}} + \underbrace{\sum_{\alpha<\beta}^{M}\frac{Z_\alpha Z_\beta e^2}{\mid \mathbf{R}_i - \mathbf{R}_j \mid}}_{\text{nuclear–nuclear interaction}} \tag{E.1}$$

To solve the full problem (eq. (E.2) in S–E) we must make some approximations to $\mathbf{H}$. A standard route is the following:

1. Assume the nuclei are at fixed positions in space. With regard to the mass difference between nuclei and electrons this is not far fetched, $m_e/M_\alpha \approx 1/2000$. This approximation is called the Born–Oppenheimer approximation. The nuclei are placed at their equilibrium positions.

2. The electrons move around in a potential that is divided into two parts. One part for the fixed nuclei V_N and an average potential V_{eff} created by the charge distribution of the electrons.

After these approximations each electron moves in the same potential, $V_N + V_{eff}$. The problem has reduced to solve the following S–E:

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + V_N + V_{eff}\right\}\phi_i = E_i\phi_i \tag{E.2}$$

There is still one difficulty left. How do we get about with V_{eff}? One way to approach the difficulty would be to say that the potential from the i-th electron is a Coulomb–potential from the charge distribution $-e \mid \phi_i(\mathbf{r}) \mid^2$. The total charge distribution is hence:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} -e \mid \phi_i(\mathbf{r}) \mid^2 \tag{E.3}$$

and for the potential V_{eff} we get:

$$V_{eff}(\mathbf{r}) = \sum_{i=1}^{N}\int \frac{e^2 \mid \phi_i(\mathbf{r}') \mid^2}{\mid \mathbf{r} - \mathbf{r}' \mid}\, d^3\mathbf{r}' \tag{E.4}$$

We are now in a position to solve the problem self consistently. We can solve eq. (E.2) if we know the potential eq. (E.4). In order to calculate V_{eff} we must however have a solution to eq. (E.2). We have here an iterative process to arrive at a solution. We have to make a guess for a starting potential V_{eff} and then just iterate and hope the process converges to a solution (it will).

Often the electrons of a crystal can be divided into two category's. From atomic physics (Bohr model) we know that for a free atom the electrons are grouped into shells. The K,

L, M,.. shells. Electrons outside filled shells are loosely bound, whereas electrons in filled inner shells are tightly bound. As we put the atoms together into a crystal, electrons in the closed shells will still be bound to their respective atoms. These electrons are localised. The outer electrons in the non filled shell (shells) are more loosely bound to the free atom and will de localise and can no longer be associated with a specific atom. The de localised electrons will form the conduction/valence bands and the localised electrons are called core–electrons.

We will use $V_N + V_{eff} = U$ as a known potential for the conduction electrons. $U(\mathbf{r})$ is periodic, $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$, where $\mathbf{R}$ is a lattice vector. In many cases (like metals) $U(\mathbf{r})$ is a weak potential (ie. the electrons are nearly free). This somewhat surprising property can be explained by two effects:

1. the core–electrons screen the nuclear potential for the conducting electrons.

2. a conducting–electron cannot come close to the nucleus due to the Pauli–principle. The volume around the nuclei is occupied by the core–electrons.

In the 1970:s it was a difficult task to perform a self consistent electron–band calculation. It was at the frontiers of research. Today's computers together with powerful software like MATLAB have rendered the calculation to a relatively simple one. Today results from band calculations are used as in data for other phenomena in crystals (photo emission, absorption, Auger–spectra, etc.).

4 Electron in a periodic potential

We will now turn to the task of actually performing the self consistent calculation. Firstly we will rewrite

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right\}\psi = E\psi \tag{E.5}$$

into a dimensionless form. Set the following

$$\frac{\hbar^2}{2ma_0^2} = 1\ , \quad a_0\ -\ \text{Bohr radius} = 0.53\ \text{Å} \tag{E.6}$$

and hence we calculate energies in units of Rydbergs (Ry)

$$1\ \text{Ry} = \frac{\hbar^2}{2ma_0^2} = 2.17 \cdot 10^{-18}\ \text{J} = 13.6\ \text{eV} \tag{E.7}$$

Now we have all energies in Ry and all lengths are measured in units of the Bohr radius. The S–E in these units will be

$$\left\{-\nabla^2 + U(\mathbf{r})\right\}\psi = E\psi \tag{E.8}$$

From $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$ we have that the potential can be written as

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \tag{E.9}$$

We will also express the wave function $\psi(\mathbf{r})$ in a Fourier–series (ie in free–electron wave functions). The $\mathbf{k}$–vectors are determined from the periodic boundary conditions

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{E.10}$$

Putting these two series (eq. (E.9) and (E.10)) into the S–E (eq. (E.8)) gives

$$\sum_{\mathbf{k}} k^2 c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} = E \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{or}$$

$$\left(k^2 - E\right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0 \tag{E.11}$$

The wave vector can take all values consistent with the periodic boundary conditions, the equation system is more or less infinite.

To solve this eigenvalue problem (eq.(E.11)) we choose a wave vector $\mathbf{k}$ in the first Brillouin zone (1BZ). The equation system eq.(E.11) relates the corresponding coefficient $c_{\mathbf{k}}$ only to coefficients $c_{\mathbf{k}-\mathbf{G}}$ with a wave vector differing by a reciprocal lattice vector $\mathbf{G}$. A set of coefficients $\{c_{\mathbf{k}-\mathbf{G}}, \mathbf{k}$ fixed in BZ, and all possible $\mathbf{G}\}$ that satisfies eq.(E.11) and all all the other $c_{\mathbf{k}'}$ vannish in the series expansion eq.(E.10) gives us a solution $\psi_{\mathbf{k}}(\mathbf{r})$. (As this solution depends on the particular choice of $\mathbf{k}$, we have to keep track of the $\mathbf{k}$.) The wave function can now be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \cdot u_{\mathbf{k}}(\mathbf{r}) \tag{E.12}$$

where

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \tag{E.13}$$

is a lattice periodic function. From the fact that the potential $U(\mathbf{r})$ and therefore the Hamiltonian is lattice periodic, we have deduced that the wave function can be written (Blochs theorem) as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \ , \quad u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r}) \tag{E.14}$$

We can no longer characterise a solution with only the wave vector $\mathbf{k}$ as for the free electron. For each $\mathbf{k}$ we can in principle assign an infinite number of solutions. We will keep track of the different solutions by ordering them according to increasing energy $\psi_{n\mathbf{k}}(\mathbf{r})$.

The Bloch–vector $\mathbf{k}$, the vector that characterises the wave–function, can always be chosen to be within the first Brillouin zone. Suppose $\mathbf{k}$ is not within the 1BZ we can always subtract a reciprocal lattice vector $\mathbf{G}$ so that $\mathbf{k}' = \mathbf{k} - \mathbf{G}$ is within the 1BZ. This operation does not change any of the results. This can easily be seen from eq. (E.12) and (E.13)

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}'} u_{\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}} = e^{-i\mathbf{G}\cdot\mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{G}'} e^{i(\mathbf{G}'+\mathbf{G})\cdot\mathbf{r}} \tag{E.15}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{G}\cdot\mathbf{r}} \cdot \sum_{\mathbf{G}'} u_{\mathbf{G}'} e^{i(\mathbf{G}'+\mathbf{G})\cdot\mathbf{r}} = e^{i\mathbf{k}'\cdot\mathbf{r}} \cdot u_{\mathbf{k}'}(\mathbf{r}) = \psi_{\mathbf{k}'}(\mathbf{r}) \tag{E.16}$$

As we see it is sufficient to study only the Bloch–vectors in the 1BZ only. The wave–function is normalised if the coefficients satisfy

$$\sum_{\mathbf{G}} \mid c_{\mathbf{k}-\mathbf{G}} \mid^2 = \frac{1}{V} \tag{E.17}$$

where V is the volume of the crystal.

In the equation system

$$\left(k^2 - E\right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0 \tag{E.18}$$

the $\mathbf{k}$ was a wave–vector that appeared in the series expansion of the wave–function. According to eq. (E.12) we can write these wave–vector like $\mathbf{k} - \mathbf{G}$, where $\mathbf{k}$ is a Bloch–vector (in the 1BZ) and $\mathbf{G}$ is a reciprocal lattice–vector. Hence it is appropriate to rewrite the equation system into

$$\left((\mathbf{k} - \mathbf{G})^2 - E_{\mathbf{k}}\right) c_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}'} U_{\mathbf{G}'-\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'} = 0 \tag{E.19}$$

where $\mathbf{k}$ is the chosen wave–vector (Bloch–vector) that characterises our solution. The Bloch–vector $\mathbf{k}$ is a 'good' quantum number and together with n it uniquely specifies the solution $\psi_{n\mathbf{k}}(\mathbf{r})$.

Conclusively the S–E eq. (E.8), with series expansions eq. (E.9) and (E.10), has been rewritten into a homogeneous equation system for the coefficients $c_{\mathbf{k}-\mathbf{G}}$. From it we can determine the energy as an eigenvalue $E_{\mathbf{k}}$ and it's associated eigenvector $c_{\mathbf{k}}$

$$\mathbf{H} c_{\mathbf{k}} = E_{\mathbf{k}} c_{\mathbf{k}} \tag{E.20}$$

and the wave–function is given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}} \tag{E.21}$$

Equations (E.8) and (E.19) are fully equivalent, and no approximations have been made so far.

Most real systems can only be solved approximately. The equation system (E.19) is of infinite dimension and can only be solved approximately. The accuracy of the solution is determined from the number of terms we have in the expansion eq. (E.21), the number of terms sets the dimension of the matrix for $\mathbf{H}$ in eq. (E.20) or (E.19).

A analysis based on a perturbation calculation shows that if the potential $U(\mathbf{r})$ is 'smooth' our approximation improves as we increase the dimension of $\mathbf{H}$. We can also from a perturbation calculation estimate the error we make. We see that eq. (E.19) reduces to the simple free–electron model if we set $U = 0$. This limiting case is called the empty–lattice approximation. For small U we expect to get good results. The general idea is that if we know the solution to a related problem – the free electron model – and regard the difference between the simple problem and our real problem as a perturbation and we investigate what changes this perturbation invokes.

Depending on the strength of the perturbation U we have two cases.

1. The perturbation is small compared to the separation between energy levels – non–degenerate perturbation calculation. In this case the free–electron solution is a good first approximation to the final solution.

2. The perturbation is large compared to the separation between energy levels – degenerate perturbation calculation. This is the case if several energy levels are degenerate or nearly degenerate, which happens if free–electron bands cross. In this case also a perturbation calculation calls upon solving an equation system. Problem H2c deals with a typical case with two degenerate energy levels.

5 Preparing for Work

In the computer exercise we solve the S–E in one dimension.

The figure shows the one dimensional band structure for the case $U = 0$, ie the empty–lattice approximation. Let k be a wave–vector within the 1BZ. All the unperturbed states, marked with open circles (o), are non–degenerate. According to Appendix a perturbation calculation gives

$$E_j = E_j^0 + \langle j \mid \mathbf{H}' \mid j \rangle + \sum_{n \neq j} \frac{\mid \langle j \mid \mathbf{H}' \mid n \rangle \mid^2}{E_j^0 - E_n^0} \tag{E.22}$$

where E_j^0 is the energy of the j-th unperturbed energy level, $\langle j \mid \mathbf{H}' \mid j \rangle$ is the matrix element of the perturbation $\mathbf{H}'$ between the unperturbed wave–functions $\mid j >$ and $\mid n >$. A lattice periodic perturbation will to first order shift all the energies by the amount of $U_{G=0}$, the expectation value for the perturbation in the unperturbed states j (if the Fourier coefficient $U_{G=0}$ is non–zero). This means a constant energy shift of the band structure. As an example in this first, lowest approximation state 3 is given by the free–electron state with wave–vector $k + 2\pi/a$.

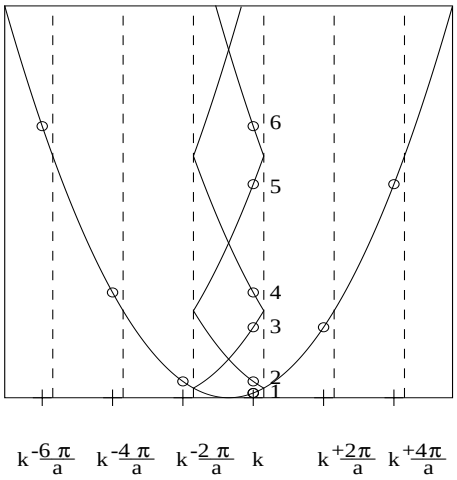

Figure E.1: The dispersion relation of a one-dimensional crystal with one atom per cell.

To second order the unperturbed states get mixed, ie the perturbed wave–functions become linear combinations of the unperturbed wave–functions, the free–electron wave–functions.

$$\mid \psi_j > \approx \mid j > + \sum_{n \neq j} \mid n > \frac{\langle n \mid \mathbf{H}' \mid j \rangle}{E_j^0 - E_n^0} \tag{E.23}$$

The perturbation calculation, second term in eq. (E.23) and third term in eq. (E.22), tells us that for a given state j the states close (in energy) to it will be the most important ones as the denominator is small for these close states. (This is true if the perturbation matrix elements in the nominator only depend weakly on n, we assume this is the case here.) In the perturbed wave–function for state 3 we expect that the free–electron wave–function for state 3 (with wave–vector $k + 2\pi/a$) will have the largest coefficient (~ 1), the coefficients for 4 ($k - 4\pi/a$) and 2 ($k - 2\pi/a$) will be smaller and even lesser for 5 ($k + 4\pi/a$) and 1 (k) and finally negligible (provided the perturbation is not to strong) for state 6 ($k - 6\pi/a$) and upwards. If we have a strong perturbation there will be more mixing among the states and we have to take more states into the series expansion eq. (E.23).. With an increasing number of terms our solution approaches the exact solution. As an approximate criterion for the exact solution we use that the energy does not change if we increase the number of terms.

6 Work

Tasks. Problems marked with a P you make at home or wherever you like you only need a **p**enciel and **p**aper for these. Problems marked with a C are intended for **c**omputers.

We will study two one–dimensional potentials.

I The cosine–potential

$$U(x) = A\left(1 - \cos\frac{2\pi}{a}x\right) \tag{E.24}$$

II The rectangular potential

$$U(x) = \begin{cases} 0 & \text{if} \quad \mid x \mid < \frac{a-\omega}{2} \\ A & \text{if} \quad \frac{a-\omega}{2} \leq \mid x \mid \leq \frac{a}{2} \end{cases} \tag{E.25}$$

You will use the programme MATLAB to solve the equation system (E.19) approximately for the two potentials given above. You determine yourself the dimension of the equation system and thereby the accuracy of the approximation for the wave–function eq. (E.21).

P1 Assume we have a one dimensional crystal with the length $N \cdot a$ where a is the lattice constant.

a) What are the k–vectors if $N = 10$? Where is the 1BZ? How many allowed k are within the 1BZ?

b) Draw the three lowest free–electron bands in the empty–lattice approximation. Determine, for $N = 10$, the energy of the highest occupied level if there are one, two or three valence electrons per primitive cell. (Within a band each k gives two states, spin up and down.)

Now we change N from being a small number into a large number.

c) Calculate the density of states (DOS) within the free–electron model.

d) Calculate the Fermi energy ϵ_F for the following three cases. Each primitive cell contributes with one, two or three valence electrons.

e) Sketch for an arbitrary k the probability distribution $\mid \psi_k(x) \mid^2$ for an electron in the three lowest bands. Use free–electron wave–functions.

f) How does the average energy for an electron in the crystal depend on ϵ_F?

P2 The one dimensional cosine potential.

a) Use the following ansatz as a solution to the S–E eq. (E.19). Construct the ansatz from three plane–waves in the series eq. (E.21)

$$\psi_k(x) = c_{k-\frac{2\pi}{a}}\, e^{i\left(k-\frac{2\pi}{a}\right)x} + c_k\, e^{ikx} + c_{k+\frac{2\pi}{a}}\, e^{i\left(k+\frac{2\pi}{a}\right)x} \tag{E.26}$$

where k is within the 1BZ. The other coefficients c are =0. Determine by use of eq. (E.19) the three lowest energies for $k = 0$. For what k is the energy minimal (ie the bottom of the band)? What is the band gap Δ_2 between band 2 and 3?

b) Determine the lowest energy for $k = 0$ with second order perturbation calculation. According to the Appendix a non–degenerate perturbation calculation gives

$$E_j = E_j^0 + \langle j \mid \mathbf{H}' \mid j \rangle + \sum_{n \neq j} \frac{\mid \langle j \mid \mathbf{H}' \mid n \rangle \mid^2}{E_j^0 - E_n^0} \tag{E.27}$$

where E_j^0 is the energy of the unperturbed j–th energy level, $\langle j \mid \mathbf{H}' \mid j \rangle$ is the matrix element of the perturbation $\mathbf{H}'$ between the unperturbed wave–functions $\mid j >$ and $\mid n >$. For the case studied here the unperturbed free–electron wave function is $\frac{1}{\sqrt{L}} e^{ikx}$, normalised over the one dimensional crystal "volume" L. Is the result consistent with the result received in a)?

c) Do the same calculation as in a) for $k = \pi/a$, but make an ansatz for ψ consisting of only two plane waves (c_k and c_{k-G}), be careful to choose the correct G. What is the band gap Δ_1 between band 1 and 2 ? Note this calculation corresponds to a degenerate perturbation calculation.

d) Why did we choose a wave function with three terms in a) but only two terms in c)?

e) A necessity for an approximation with just a few plane waves to give any decent results is that the amplitude A of the perturbation is small. Assume that the two lowest bands and the the two lowest band gaps Δ_1 and Δ_2 are to be determined such that the error in energy is less than δE. (An error in energy arises because we have neglected higher free–electron bands in the expansion of the wave–function. If we neglect, as we have done here, the fourth free–electron band we might not expect that energies in the third band are that correct especially not in the upper part.) Estimate for what A the calculation in a) and c) give an acceptable approximation of the energy, in the range from the bottom of the band up to Δ_2. Estimate an upper boundary A_{max} for A that makes the error in energy less than an acceptable δE if $A < A_{max}$. (δE you choose yourself, you may take 0.1Ry.)
Make a choice of the lattice constant a (typical lattice constants are in the range 5–10 Bohr radius). Draw the three energies determined in a) at $k = 0$ and the two energies determined in c) at $k = \pi/a$ as a function of A. Use both values the are under and above A_{max}.

C3 Now we start to use MATLAB, on cosine potential.

a) Choose an $A << A_{max}$ from the figure you made previously. Use three ($k = 0$) plane waves and calculate the energies numerically with MATLAB. Repeat the same for $k = \pi/a$. Do the numerical results corroborate your previous results?

b) Choose an $A \sim A_{max}$ and increase the number of plane waves ie increase the dimension NDIM of the matrix. What is the lowest value of NDIM where a further increase will not change the results for the energy? This solution corresponds to the exact solution.

c) Calculate with MATLAB, for the same A as in P2e, the exact energies and draw these in the same figure as in P2e. When do the "exact" energies start to deviate from your earlier results in P2e? Was your estimate of A_{max} you made in P2e correct?

C4 Continuation on MATLAB, on rectangular potential.

a) Choose a barrier width $\omega \neq a/2$e in the rectangular potential and use the same a as you did in P2 and C3. Calculate, with MATLAB, for some small A the band gaps Δ_1 and Δ_2. Compare your results between the two potentials: how do the band gaps depend on A, are they linear in A or are they like A^2? What may cause the difference between the two cases?

C5 Continuation on rectangular potential.

a) Choose a decently large value for A, such that only a few coefficients c_k are clearly nonzero and rest are small or zero. Study the wave–functions (coefficients of the series expansion) at $k = 0$ and $k = \pi/a$ and sketch the electron probability distribution $\mid \psi_k(x) \mid^2$. How can we understand that a band gap occurs at $k = \pi/a$ (see CK p 177f / HH 4.1)?

b) Show for a k (close to the BZ–edge) that the expectation value of the velocity $< v >$ ($\sim$ group velocity v_g) is given by

$$\langle v \rangle = \frac{1}{\hbar} \frac{\partial E}{\partial k} \tag{E.28}$$

by first:

i) Calculate the quantum–mechanical expectation value of the momentum operator $\mathbf{p}$ with the numerically determined coefficients

$$\langle \psi_k \mid \mathbf{p} \mid \psi_k \rangle = \sum_G \sum_{G'} c^*_{k-G} c_{k-G'} \int e^{-i(k-G)x} (-i\hbar) i(k-G') e^{i(k-G')x} \, dx$$
$$= \sum_G \hbar(k-G) \mid c_{k-G} \mid^2 \tag{E.29}$$

ii) and after this calculate the derivative $\frac{\partial E}{\partial k}$ numerically. (Calculate $\langle v \rangle$ in m/s.)
Note units! MATLAB normalises according to

$$\sum_G \mid c_{k-G} \mid^2 = 1 \tag{E.30}$$

Equation (E.29) assumes normalising according to eq. (E.17).

c) Draw a graph of $\langle v \rangle$ as a function of k for the two lowest bands. What happens at the BZ–edge?

d) Calculate

$$m^* = \left\{ \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2} \right\}^{-1} \tag{E.31}$$

by an explicit calculation of the second derivative and plot m^*/m as a function of k for the two lowest bands.

Now we let A become larger and larger. The dimension NDIM of the matrix should be adjusted in such a way that errors in the energy do not exceed $\sim$1%.

C6) Study the band gaps Δ_1 and Δ_2 as a function of A. What happens to the bands as A increases? Draw graphs of the bands for some different values of A. What happens to the velocities and effective masses? What happens to the width of the bands?

P7) Predict the energies for the three lowest bands in the limit $A \to \infty$ sketch the probability distribution of the electrons in this case.

C8) Compare with a numerical calculation.

The dependence of the band structure on A in our model problem can be interpreted in the following way. For $A \to \infty$ the barriers between the atoms become very large, the electrons become localised, and hence the electrons are bound to the atoms. The probability for an electron to tunnel from one atom to another atom is negligible, the effective mass is infinitely large. As the barrier height decreases the localised electron wave–functions begin to overlap, electrons begin to tunnel from atom to atom , the localised wave–functions begin to de localise and the effective mass decreases, electrons move more easily. Finally as $A \to 0$ we regain the free-electron picture. This interpretation corresponds to what happens as we put together atoms into a crystal. The correspondence is not exact as for putting real atoms together we both change the height and the width of the potential, whereas in our model we have only changed the height and kept the width constant. Both case however give qualitatively similar results.

7 Appendix: Time independent perturbation calculation

In quantum mechanics one often encounters a problem (with Hamilton operator $\mathbf{H}$) that we cannot solve exactly. In many cases however we have a solution to a simpler ($\mathbf{H^0}$), but related problem

$$\mathbf{H^0}\psi_p^0 = E_p^0\psi_p^0 \tag{E.32}$$

(We assume for simplicity that the eigenvalue spectrum for the Hamilton operator $\mathbf{H^0}$ is discrete, which also applies to $\mathbf{H}$) if the perturbation is small.) We try to split the the Hamilton operator $\mathbf{H}$ of the full problem into two parts

$$\mathbf{H} = \mathbf{H^0} + \mathbf{H'} \tag{E.33}$$

where $\mathbf{H'}$ in some sense is small and can be treated as a weak perturbation of the unperturbed Hamilton operator $\mathbf{H^0}$. Let $\mathbf{H'}$ be proportional to a parameter λ, a coupling constant that represents the strength of the perturbation. Further we assume, that eigenvalues E and eigen functions ψ of our problem

$$\mathbf{H}\psi = E\psi \tag{E.34}$$

can be written as a power series in λ. Up to second order in λ one finds for the eigenvalue E_j, that corresponds to the unperturbed eigenvalues E_j^0

$$E_j = E_j^0 + \langle j \mid \mathbf{H'} \mid j\rangle + \sum_{n\neq j} \frac{\mid \langle j \mid \mathbf{H'} \mid n\rangle \mid^2}{E_j^0 - E_n^0}. \tag{E.35}$$

The matrix element of the perturbation can also be written like

$$\langle j \mid \mathbf{H}' \mid n \rangle = \int_0^L \psi_j^{0*}(x) \mid \mathbf{H}' \mid \psi_n^0(x)\, dx. \tag{E.36}$$

The first order term

$$\langle j \mid \mathbf{H}' \mid j \rangle \tag{E.37}$$

is the expectation value of the perturbation $\mathbf{H}'$ on the unperturbed state. To lowest order (=first) the energy of a state may change but the wave–function is still given by the unperturbed wave–function.

The perturbation will however also effect the wave–functions to lowest order these will be

$$\mid \psi_j > \approx \mid j > + \sum_{n \neq j} \mid n > \frac{\langle n \mid \mathbf{H}' \mid j \rangle}{E_j^0 - E_n^0}. \tag{E.38}$$

The perturbed state $\mid \psi_j >$ will contain not only the unperturbed state $\mid j >$ but there will also be mixing with other unperturbed states $\mid n >$. This correction of the wave–function gives rise to the second order term in (third term) eq. (E.22,E.35). This term shows that the effect of state $\mid n >$ with energy E_n^0 diminishes as the energy difference to E_j^0 increases. (This assumes that matrix elements of the perturbation is a relatively "smooth" function.) The second order term also shows that this procedure does not work if there is degeneracy, ie the denominator will become zero in this case. If there is degeneracy a the procedure for a perturbation calculation goes very much along the lines described in the numerical part of this computer lab.

8 Credits

This material has evolved from a similar computer lab session developed by Günter Grossman, Department of Solid State Physics, Lund University.

F

Lab: Magnetism

1 Purpose

The purpose of this lab session is to measure the paramagnetic susceptibility χ of some salts and Aluminium with Gouy's method.
Keywords: Magnetism, para magnetism, dia magnetism, ferro magnetism, Gouy's method.

2 Literature

C. Kittel, Introduction to Solid State Physics, chapter 14 and 15,
J.R. Hook and H.E. Hall, Solid State Physics: chapter 7 and 8.

3 Magnetic properties

The earliest known application of magnetism is the compass, known to the chinese. The origin of the word magnetism is however from Greece: 'lithos Magnetes' means stone from Magnesia, a province in Greece. Since the 19th century we are familiar with more important applications of magnetism like: electrical engines, transformers, generators and the hard disc of computer just to mention a few.

The magnetic properties of a material are described by the magnetic susceptibility χ, CK page 417 eq (14.1) or HH eq (7.1). With it we can make the following classification of magnetic materials.

- For a **diamagnetic** material we have $\chi < 0$ and for a **paramagnetic** material we have $\chi > 0$.
- For a **ferromagnetic** material there is no proportionality between M and B and $\chi >> 0$ is not a well defined property.
- Other kinds of magnetism are **antiferromagnetism** and **ferrimagnetism**.

The different kinds of magnetism are described in more detail in chapter 14 in CK and chapters 7 and 8 in HH.

The purpose of this laboratory exercise is to measure the magnetic susceptibility of some paramagnetic and diamagnetic substances. The substances are aluminium and the following salts $CuCl_2 \cdot 2\ H_2O$, $CuSO_4 \cdot 5\ H_2O$, $FeSO_4 \cdot 7\ H_2O$, $NiSO_4 \cdot 6\ H_2O$, $MnCl_2 \cdot 2\ H_2O$ and $Ce(NO_3)_3 \cdot 6\ H_2O$.

4 Diamagnetism

The physical mechanism of diamagnetism (CK page 417–420) can be described with Lenz law. When the magnetic flux is changed in an electric circuit, an electric current is induced in such a way as to counteract the applied change in flux. The induced magnetic flux is directed opposite to the applied flux and hence the susceptibility is negative, see CK page 418 or HH eq 7.39. Diamagnetism is present in general but it is a very weak effect and can be observed in cases where the atoms do not have a strong permanent magnetic moment.

5 Paramagnetism

The physical mechanism of paramagnetism (CK page 420–429, HH page 198–211) is that the material contains permanent magnetic moments (in molecules, atoms, ions or electrons). In the salts we use here the magnetic moments arrise from the metal ions in the salts, the metal ions have partially filled shells and hence a net magnetic moment. These microscopic magnetic dipoles are usually randomly oriented. Hence there total magnetic moment adds up to zero. The sample will respond to an external magnetic field in such a way that the magnetic dipoles will tend to align along the field. The phonons on the other hand will try to disalign them. So there is a competition between these two effects, the thermal disorientation and the organising external field. A calculation of the paramagnetic susceptibility of atoms or ions in a solid gives $\chi \propto 1/T$, **Curies law**, see page 422 (eq 22) in CK or eq 7.18 and 22 in HH.

$$\chi = \frac{np^2\mu_B^2}{3k_BT}\mu_0 \tag{F.1}$$

Where n is the density of the ion in question. The expression for χ also contains the quantity $p = g\sqrt{J(J+1)}$, the effective number of Bohr magnetons. If we know g and J a theoretical value for p can be calculated.

By measuring the susceptibility χ we can also estimate an experimental value for p. A comparison of the two p values gives information on angular momentum coupling. Landé's g–factor can be calculated by (CK page 420 (eq 13) or HH eq 7.10 and eq(13))

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{F.2}$$

where L is the total orbital angular momentum and S is the total spin. The quantum numbers can be determined by the use of Hund's rules, CK page 424 or HH page 201. The problem below illustrates how the connection of L, S and J works and how to apply Hund's rules.

Problem 1

1.1 How many electrons can at maximum be placed in a d–shell?

1.2 Determine with Hund's rules the quantum numbers J, L and S for the following electron configurations: $3d^9$, $3d^8$, $3d^6$, $3d^5$ and 4f ($= 4f^1$) ?

1.3 What theoretical p–values do you get for the electron configurations above ?

1.4 In some cases we have "quenching" of the orbital angular momentum (CK page 426). This means that $L = 0$. What values for p do you get if "quenching" occurs?

For non–ferromagnetic metals (like Aluminium) Curie's law does not apply for the susceptibility (see CK page 433–436 or HH 7.2.4). An experimental study of the temperature dependence one finds that χ is nearly independent of temperature. One also finds that the experimental values are a factor of 100 less than an estimate from Curie's law. This is because for the electron gas in a metal one has to use the Fermi–Dirac distribution.

Besides the paramagnetic susceptibility there is also a diamagnetic contribution (Landau–magnetism) due to the free electron orbits. The susceptibility of the electron gas is given by eq 43 page 436 in CK or eq 7.23 and 7.24 in HH.

$$\chi = \frac{n\mu_B^2}{k_B T_F}\mu_0 \tag{F.3}$$

6 Gouy's method

A determination of the susceptibility is done by measuring the force exerted by an inhomogeneous magnetic field on our sample. The force is extremely small and we have to use a very sensitive method. In the experiment we make use of Gouy's method. In it the sample is freely suspended in an inhomogeneous magnetic field according to figure F.1.

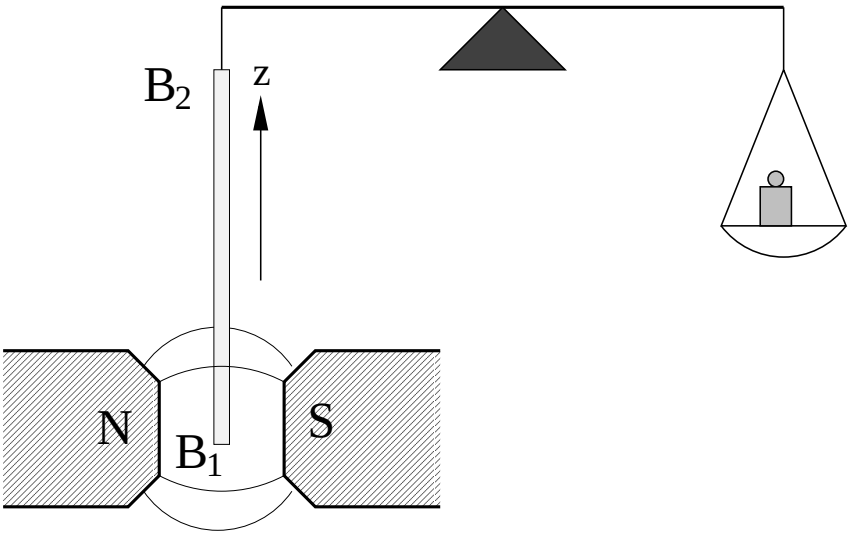

Figure F.1: Gouy's method to determine the susceptibility

Figure F.2: Gouy's method real life showing electro magnets and sample between them. The sample is hanging on a thin wire entering the experimental area through a hole in the upper concrete slab.

In an inhomogeneous magnetic field the atomic dipoles are attracted towards the stronger field if the material is paramagnetic and the is repelled out of the stronger field if it is diamagnetic. The force F on the sample can be calculated from

$$F = -\nabla U \tag{F.4}$$

where U is the potential energy of a magnetic dipole μ in a magnetic field B:

$$U = -\mu \cdot B \tag{F.5}$$

The magnetic field B is applied in the x–direction, perpendicular to the z–direction. The sample is a thin long rod or a glass tube containing the salt, in the z–direction arranged in such a way that one end is at B_1, where the magnetic field has its maximum. Let A be the cross sectional area of the sample. The incremental volume element $A\ dz$ of the sample is in a homogeneous magnetic field (dz is very thin). The incremental contribution to the magnetic energy will be

$$dF_z = \frac{A\ dz\ \chi\ \frac{\partial B_x^2}{\partial z}}{2\mu_0} \tag{F.6}$$

Where A is the cross sectional area of the sample. Integrating along the sample in the z direction will give the total force F_z in the z direction

$$F_z = -\frac{A\ \chi\ (B_1^2 - B_2^2)}{2\mu_0} \tag{F.7}$$

where B_1 and B_2 are the magnetic fields at the lower and upper end of the sample. (Often B_2 can be neglected in comparison with B_1.)

Problem 2

2.1 If the change in the weight with or without magnetic field on the weight scale is Δm , what is the relation you get for the susceptibility in terms of Δm?

7 Doing the experiment

The following steps you have to do in order to perform an experiment:

1. Calibration of the magnets.
2. Measure Δm versus current I for the six salts and the Aluminium rod.
3. analyse your results.

Calibrating the equipment. The maximum current you may put through the electro magnets is $I_{max} = 0.75$A, if you exceed this current the magnets will get to hot and may be damaged.

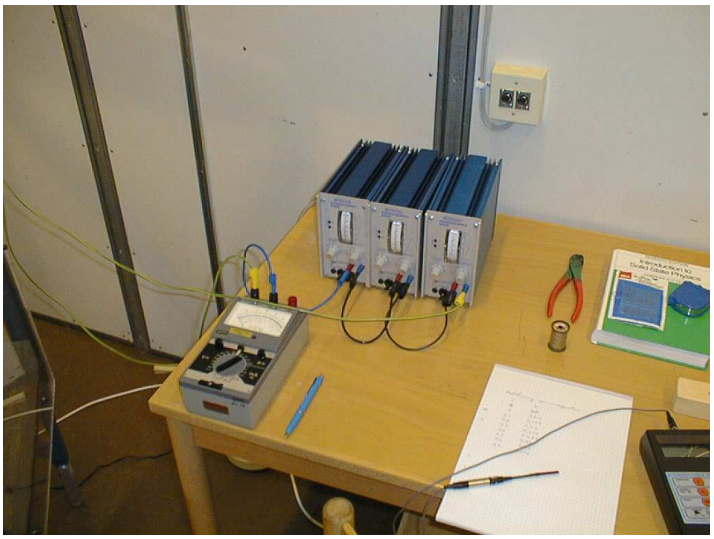

Figure F.3: The three Oltronix power supplies

The power supply to the electro magnets is from three Oltronix (B200) power supplies coupled in series see figure F.3. You have to turn on power on all three and you operate the output by adjusting the three voltage knobs (the one to the right on the instrument). There are red lamps on them and the one marked 'CV' must be alight. If the lamp marked 'CC' turns on it indicates an overload and you have to reduce the output in order to turn the 'CC' lamp off and the 'CV' lamp on again. This might happen if there is a large unbalance between the three units and it is therefore good practice to let the output from the units roughly be on the same level. The voltage output is the right scale on the Oltronix unit.

The current through the electro magnets is read of from the separate amp–meter (Unigor 5p).

Before you start doing any measurements of Δm you have to determine the relation between the current I through the electromagnets and the magnetic field B_1 in the centre of the gap, see figure F.1. Do not remove the electro magnets out from the experimental setup to perform your calibration see figure F.4. To do the calibration you have a magnetometer (F.W. Bell, instruction at lab site), based on the Hall effect. Make a graph

on millimetre paper, also available at the lab site, of the magnetic field B_1 as a function of the current I through the electromagnets. Use something like 6 to 8 evenly spaced currents in the range from 0 A to 0.75 A.

You can check that your calibration curve is reasonable. At the lab site you have a copy of technical specification of the magnets. The gap we use is something like 11 millimetres.

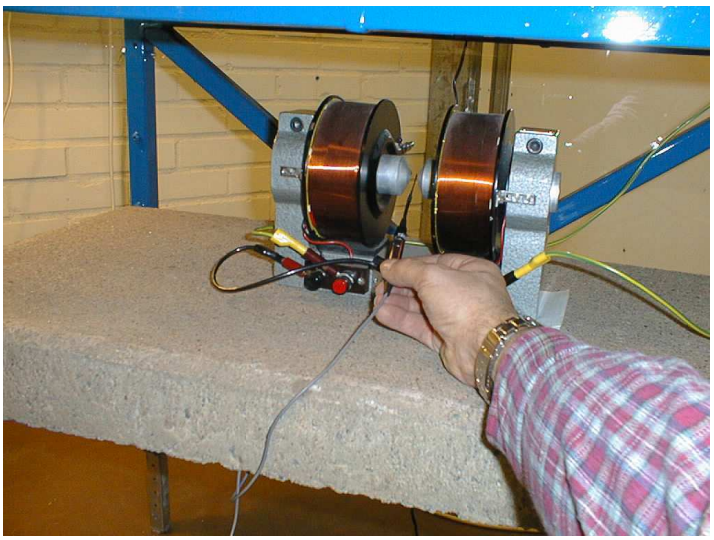

Figure F.4: Calibrating the magnets with magnets in the experimental area

Measure Δm versus current I for the samples and an empty tube The change of mass Δm you read of from an Sartorius scale see figure F.5.

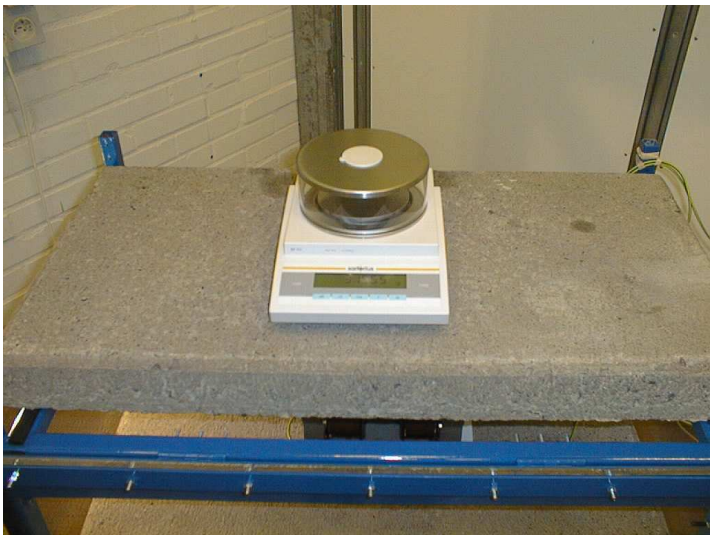

Figure F.5: Sartorius scale

Next to the scale is an instruction on how to change between standby mode and active mode.

The scale stands on a concrete stone, and the sample hangs on a thin wire under the scale. A hole has been drilled through the concrete stone to let the thin wire enter inte

the area where the electro magnets are. **Do not move the Sartorius scale around as the thin wire might disengage from the scale**. There will not be any irreparable damage, but it may take a while to align the equipment again.

On a second concrete stone below the first one the electro magnets are standing. As you hang a sample onto the hook on the thin wire from scale it might be that you have to move the magnets a tiny bit to make sure that the sample is in the centre of the gap.

As you have placed the sample in position close the front lid (to stop air movements) and push the 'tare' button on the Sartorius scale as you do this the current through the electro magnets **must be zero** do this by turning of the Oltronix power supplies. After this you are ready to make your measurements.

Problem 3 Data for the salts are give below (at the end and some data you find at the lab site)

3.1. For seven samples: aluminium and the salts $CuCl_2$, $CuSO_4$, $FeSO_4$, $NiSO_4$, $MnCl_2$ and $Ce(NO_3)_3$. measure the weight Δm as a function of B_1 and present your results as graphs of Δm vs B_1^2. Do the same for the empty tube as the tube will also have a small contribution to χ.

3.2. How is the measurement of Δm above influenced by the susceptibility of the glass tube?

3.3. From the slope of the graphs calculate the susceptibility of the seven samples. Use the extra empty tube an the vernier calliper (skjutmått) to calculate the cross sectional area A of the samples. We assume that all glass tubes have the same inner diameter.

3.4. Use the χ you have determined for aluminum to calculate the fermi energy of the electron gas. Assume that every Al – atom has three electrons and use the free–electron model.

3.5. Calculate for the chosen salt the number of effective Bohr magnetons.

3.6. Compare your result above with a theoretical calculation. Which salts have a quenched orbital angular momentum?

Data for the salts, molar weights you find on the bottles containing the chemicals. These are available at the lab site:

Salt	density ρ 10^3 kg/m^3	ion	configuration	molar weight
$CuCl_2 \cdot 2\ H_2O$	1.18	Cu^{2+}	$3d^9$	
$CuSO_4 \cdot 5\ H_2O$	1.26	Cu^{2+}	$3d^9$	
$FeSO_4 \cdot 7\ H_2O$	1.13	Fe^{2+}	$3d^6$	
$NiSO_4 \cdot 6\ H_2O$	1.09	Ni^{2+}	$3d^8$	
$MnCl_2 \cdot 2\ H_2O$	1.07	Mn^{2+}	$3d^5$	
$Ce(NO_3)_3 \cdot 6\ H_2O$	1.40	Ce^{3+}	4f	

Lab report has to contain:

Answers to problems 1 – 3.

The graphs including calibration graph.

In case needed supplementary explanations.